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VOL. XXV. [JANUARY, 1903.] NO. 1.

THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

BY F. W. CLARKE.

Received November 21, 1902.

IN the year 1900 an international committee on atomic weights was organized, composed of more than fifty representatives from chemical and other societies. Its conferences were necessarily conducted by correspondence, and the delays and difficulties of the work proved to be both serious and annoying. Accordingly, the committee, by vote, designated a smaller body of three representatives, and the latter now has the honor to report its recommendations.

On the fundamental question of standards, definite and formal action seems to be impracticable. By the original committee of the German Chemical Society the oxygen standard was adopted, but that proposal, while receiving strong support, also met with serious opposition. In fact, opinion, as expressed by individual voices, seems to be somewhat evenly divided upon this question, and around it there has already grown up a controversial literature of formidable proportions. To force the adoption of either standard, oxygen or hydrogen, appears therefore to be impossible, and for some time to come both are likely to be employed. Between them, experience must be the final arbiter. That standard

which best serves to coördinate chemical and physical knowledge will ultimately be chosen, and the other will gradually fall into disuse. Meanwhile, it is important that the most probable values for the several atomic weights should be indicated, and that every table of them should be consistent within itself. Such a table has been prepared by our distinguished predecessors, and its revision, as knowledge advances, seems to be our proper function.

In order that our work may be of the most general service, we have prepared a table in which both standards of atomic weight are represented. In most of its details it is identical with the table which was reported by the previous committee at the beginning of the year 1902.[1] Some changes, however, have in our judgment become necessary, and these may be briefly indicated as follows: when O = 16.

Antimony. In the former reports of the Committee, the value derived by Cooke from analyses of the bromide, Sb = 120, was adopted. This, however, ignores the work of Cooke and of Schneider upon antimony trisulphide, and the still more recent determinations made by Friend and Smith. The true number being therefore in doubt, we recommend the use of an average value, and put Sb = 120.2.

Germanium. The number 72.5 is more nearly in accord with Winkler's determinations than the former number 72.

Hydrogen. In the column which represents the oxygen standard, hydrogen has heretofore been assigned the value 1.01. The number 1.008 is, however, much more exact, and the error in 1.01 is too large to be perpetuated. Each figure should be given to the nearest *significant* decimal.

Lanthanum. During 1902 two new determinations of the atomic weight of lanthanum were published. According to Jones, La = 138.77. Brauner and Pavlicek found La = 139.04. Both investigations were conducted with great skill and care, and each one seems to have some points of advantage over the other. The average, La = 138.9, appears to be the safest value to adopt. These data naturally influence our judgment in the case of cerium, and we retain the Brauner number, Ce = 140, rather than adopt the lower estimates made by other observers.

Mercury. Taking into account all of the determinations which

[1] In No. 1 of the *Berichte*, for 1902.

have appeared, and giving great weight to the most recent measurements by Hardin, we regard the value Hg = 200 as best warranted by the existing evidence.

Palladium. The atomic weight of this metal is in doubt. The best determinations give values ranging from 106 to 107. The mean between them, Pd = 106.5, has been provisionally adopted.

Radium. This element appears in the table for the first time. Madame Curie's determination of the atomic weight, Rd = 225, is probably not far from the truth.

Selenium. Judging from the work of Lenher, and the very recent determinations by Meyer, the former value, Se = 79.1, is probably too low. In order to give due weight to the newer measurements we write Se = 79.2.

Tin. The determinations by Bongartz and Classen, which seem to be the best, make Sn = 119. The former value, 118.5, is almost certainly too low.

Uranium. According to the very recent investigation by Richards and Merigold, U = 238.5.

Zirconium. The figure Zr = 90.6 is apparently the most probable.

In thus assuming the duties assigned to us by the larger International Commission, we act upon the conviction that the purpose of our appointment is to secure the promptness and efficiency which is only possible with a comparatively small working body. In order to carry out this purpose, we must depend upon the coöperation and assistance of our colleagues. We therefore beg that they, and all other chemists who are interested in researches upon atomic weights, will aid us with their criticisms and advice. We especially ask that publications upon the subject shall be sent to us, in triplicate if possible, so that no matter of importance may be overlooked. Without support of this kind our work cannot be made fully effective.

The complete table of atomic weights, with the foregoing changes incorporated, follows:

F. W. CLARKE,
T. E. THORPE,
KARL SEUBERT,
Committee.

1903.

INTERNATIONAL ATOMIC WEIGHTS.

		O = 16.	H = 1.
Aluminum	Al	27.1	26.9
Antimony	Sb	120.2	119.3
Argon	A	39.9	39.6
Arsenic	As	75.0	74.4
Barium	Ba	137.4	136.4
Bismuth	Bi	208.5	206.9
Boron	B	11.	10.9
Bromine	Br	79.96	79.36
Cadmium	Cd	112.4	111.6
Caesium	Cs	133.	132.
Calcium	Ca	40.1	39.8
Carbon	C	12.00	11.91
Cerium	Ce	140.	139.
Chlorine	Cl	35.45	35.18
Chromium	Cr	52.1	51.7
Cobalt	Co	59.0	58.56
Columbium	Cb	94.	93.3
Copper	Cu	63.6	63.1
Erbium	Er	166.	164.8
Fluorine	F	19.	18.9
Gadolinium	Gd	156.	155.
Gallium	Ga	70.	69.5
Germanium	Ge	72.5	71.9
Glucinum	Gl	9.1	9.03
Gold	Au	197.2	195.7
Helium	He	4.	4.
Hydrogen	H	1.008	1.000
Indium	In	114.	113.1
Iodine	I	126.85	125.90
Iridium	Ir	193.0	191.5
Iron	Fe	55.9	55.5
Krypton	Kr	81.8	81.2
Lanthanum	La	138.9	137.9
Lead	Pb	206.9	205.35
Lithium	Li	7.03	6.98
Magnesium	Mg	24.36	24.18
Manganese	Mn	55.0	54.6
Mercury	Hg	200.0	198.5
Molybdenum	Mo	96.0	95.3
Neodymium	Nd	143.6	142.5
Neon	Ne	20.	19.9
Nickel	Ni	58.7	58.3
Nitrogen	N	14.04	13.93

		O = 16.	H = 1.
Osmium	Os	191.	189.6
Oxygen.....	O	16.00	15.88
Palladium	Pd	106.5	105.7
Phosphorus	P	31.0	30.77
Platinum	Pt	194.8	193.3
Potassium	K	39.15	38.86
Praseodymium .	Pr	140.5	139.4
Radium	Rd	225.	223.3
Rhodium	Rh	103.0	102.2
Rubidium.....	Rb	85.4	84.8
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.	148.9
Scandium.....	Sc	44.1	43.8
Selenium	Se	79.2	78.6
Silicon.....	Si	28.4	28.2
Silver.....	Ag	107.93	107.12
Sodium	Na	23.05	22.88
Strontium.....	Sr	87.6	86.94
Sulphur	S	32.06	31.83
Tantalum.....	Ta	183.	181.6
Tellurium	Te	127.6	126.6
Terbium.....	Tb	160.	158.8
Thallium	Tl	204.1	202.6
Thorium.....	Th	232.5	230.8
Thulium.....	Tm	171.	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten.....	W	184.	182.6
Uranium.....	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon.....	Xe	128.	127.
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc.....	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

[CONTRIBUTIONS FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

VIII. SOME CUBAN SOILS OF CHEMICAL INTEREST.

BY WM. FREAR AND C. P. BEISTLE.

Received October 18, 1902.

SOME time since, the writer received from Mr. Luis Marx, a Cuban tobacco grower, samples of a deep red soil from the

plantations San Antonio and Zorilla, in the municipality of Alquizar, in the southwestern part of the province of Havana. The results of the physical and chemical examination of these soils made by Mr. C. P. Beistle, under the direction of the writer, exhibit some peculiarities worthy of notice.

These soils were described as nearly virgin, deep and only slightly stony, and of a calcareous clay nature. The land lies high, is level, very permeable and never shows excess of standing water. The land is highly fertile, producing large crops of fine-leafed, elastic tobacco, numerous grasses and palms.

Dr. C. W. Hayes, of the United States Geological Survey, who recently made a reconnoissance of Cuba, states, in a letter to the writer, that the soils of the southern part of the province of Havana have a deep red color, and lie upon a horizontal or very gently undulating plain of subaerial denudation. No true coral reef rock has been noted in this part of the province, the larger part, probably, of the soil of this district being derived from a soft, friable chalk or chalky marl, though part of the limestone is a hard rock, projecting in angular points and weathered into a cavernous surface. The geological age of these rocks is not definitely ascertained; they are of a tertiary formation, probably corresponding to the Oligocene of the United States.

The soils considered in this paper have received no manurial application. The "surface" soils represent the upper twelve inches; the depth represented by the "subsoils" is not stated. The samples had been carefully sifted to remove coarse particles, before shipment.

SPECIFIC GRAVITY.

The specific gravity was determined by the usual pycnometric method, with results as follows:

	Specific gravity, $\frac{15.6^\circ\ C.}{15.6^\circ\ C.}$
San Antonio :	
Surface soil	2.677
Subsoil	2.681
Zorilla :	
Surface soil	2.714
Subsoil	2.711

The large amount of iron present is sufficient to account for

the rather high specific gravity. That there is little difference between the so-called surface and subsoils, is in accord with the fact that they are of similar color.

MECHANICAL ANALYSIS.

The subsoils were subjected to mechanical analysis by the Osborne beaker method, a tap-water of very slight alkalinity being used.

	San Antonio. Per cent.	Zorilla. Per cent.
Gravel (2–1 mm.)	....	....
Coarse sand (1–0.5 mm.)	1.23	10.78
Medium sand (0.5–0.25 mm.)	13.63	12.75
Fine sand (0.25–0.1 mm.) / Very fine sand (0.1–0.05 mm.)	32.80	30.84
Silt (0.05–0.01 mm.)	17.79	13.69
Fine silt (0.01–0.005 mm.) / Clay (less than 0.005 mm.)	15.10	12.72
Loss upon ignition (organic matter, combined water, etc.)	19.45	19.22
	100.00	100.00

About five-eighths of the water-free soil (residue from ignition) belongs to the group of 'sand,' while the 'clay' constitutes less, probably, than one-eighth of the whole.

This state of subdivision should produce the permeable texture and ready drainage said to mark the soils in place.

While these figures well represent the present condition of these soils, the use of a deflocculating agent like the 4 per cent. ammonia water used for the determination of 'active humus' or *matière noire* led to a complete breaking down of the 'sandy' particles into the finest clay. So fine were these particles that 70 per cent. or upwards of the mineral matter in the several soils passed through double parchment filters and a clear filtrate was obtained only by use of a Pasteur filter. The apparently sandy or loamy condition of these soils at the present time is doubtless attributable to the flocculant action of the carbonates of lime and magnesia present.

CHEMICAL ANALYSIS.

The soils were analyzed by the methods of the Association of Official Agricultural Chemists, the acid solution being, however,

subjected to a greater number of evaporations and re-extractions to assure the complete removal of silica therefrom. The means of closely concordant, duplicate determinations are given in the following table:

CHEMICAL ANALYSES OF CUBAN SOILS.

	San Antonio. Surface. Per cent.	San Antonio. Subsoil. Per cent.	Zorilla. Surface. Per cent.	Zorilla. Subsoil. Per cent.
Moisture (loss at 100° C. in water-oven)	1.42	2.58	0.57	0.81
(Composition of water-free soils.)				
Acid insoluble (not decomposed)	7.420	15.910	15.930	13.050
Soluble silica (dissolved by Na_2CO_3 solution)	27.080	19.820	17.450	19.690
Potash	0.190	0.110	0.165	0.155
Soda	0.140	0.135	0.220	0.210
Lime	0.270	0.370	0.350	0.370
Magnesia	0.190	0.140	0.210	0.130
Mangano-manganic oxide	0.118	0.086	0.070	0.081
Ferric oxide	16.630	15.750	17.150	17.490
Alumina	27.860	29.350	28.255	29.270
Phosphoric acid	0.555	0.470	0.475	0.440
Sulphuric acid	0.035	0.065	0.060	0.030
Carbonic acid	0.555	0.315	0.275	0.305
Chlorine	trace	trace	trace	0.000
Loss on ignition, corrected for CO_2 expelled	18.912	16.808	19.566	18.930
	99.955	99.329	100.176	100.151
Phosphoric acid soluble in citric acid (1 per cent)	0.0087	0.0065	0.0060	0.0055
Potash soluble in citric acid (1 per cent.)	0.0098	0.0104	0.0125	0.0094
Nitrogen	0.255	0.145	0.230	0.165
Organic carbon	2.502	1.349	2.802	2.091
Organic matter corresponding (C × 1.724)	4.313	2.326	4.831	3.605
Water of combination:				
(*a*) Loss on ignition (corrected), less hygroscopic moisture and organic matter	14.599	14.482	14.735	15.325
(*b*) Total water obtained by combustion, less hygroscopic moisture and water derived from organic matter (assumed to contain 5 per cent. of hydrogen)	15.249	15.331	14.484	13.723

Organic matter was determined by the method described by Van Bemmelen,[1] except that the hygroscopic moisture was de-

[1] *Landw. Versuchs-Sta.*, **37**, 279.

termined by the official method, instead of by drying *in vacuo* over sulphuric acid, as Van Bemmelen prefers.

The surface soils are distinctly richer in organic matter than the subsoils. There are not a very large number of recent analyses by this method on record for comparison. Van Bemmelen[1] found 2.65 to 5.07 per cent. in certain clay soils of Java and Sumatra. Warington and Peake[2] found as much as 6.12 per cent. in an old pasture and as little as 0.65 per cent. in a clay subsoil. E. H. Hess,[3] working under direction of the writer, found in the limestone clay lands of the Pennsylvania Experiment Station, from 2.53 to 3.09 per cent. according to their manurial treatment. These few data warrant the opinion, however, that these virgin Cuban soils contain rather more humus than the more worn clay lands of the humid region contain.

Owing to the impossibility of eliminating the water of combination of the large amount of mineral matter associated with the active humus in its ammoniacal solution, the separate determination of this part of the organic substance was given up.

The soils contain very little sulphur and chlorine and probably little ferrous iron. It may therefore be assumed that the loss upon ignition of the "water-free" soil represents quite accurately the result of destruction of the organic matter and the expulsion of water combined with the organic materials and the hydrous minerals. The combined water has been estimated by direct subtraction of the computed organic matter from the total loss upon ignition. A check computation has been made, based upon the total moisture obtained upon combustion, corrected for hygroscopic moisture; from this total, there was subtracted the water corresponding to the hydrogen of the organic matter, which was assumed, after Van Bemmelen,[4] to contain 5 per cent. of this element. The results by the two methods differ beyond the limits of analytical error, thus failing to exhibit the surprising agreement that Van Bemmelen obtained in a variety of soils upon application of these methods.

The foregoing data are of especial interest in considering these soils as the products of certain geological processes. From this

[1] *Loc. cit.*
[2] Cited by Wiley, "Principles and Practice of Agricultural Analysis," Vol. I, p. 323.
[3] Proc. Soc. Prom. Agr. Science, 1900.
[4] *Loc. cit.*

point of view the extensive decomposition effected by the action of hot hydrochloric acid is especially significant. It is emphasized by the following tabular statement:

	San Antonio.		Zorilla.	
	Surface. Per cent.	Subsoil. Per cent.	Surface. Per cent.	Subsoil. Per cent.
Undecomposed mineral matter, insoluble in HCl and Na_2CO_3 solution...	7.420	15.910	15.930	13.050
Decomposed mineral matter:				
Gelatinous silica..	27.080	19.820	17.450	19.690
Dissolved in HCl.	46.088	46.476	46.955	48.176
Carbon dioxide...	0.555	0.315	0.275	0.305
Water of combination (*a*).....	14.599	14.482	14.735	15.325
	88.222	81.093	79.415	83.496
Organic matter.....	4.313	2.326	4.831	3.605
	99.955	99.329	100.176	100.151

The high solubility observed, is clearly not due, as in highly calcareous soils, to the presence of large quantities of calcite, magnesite or gypsum. It appears to be partially explained by the large amounts of iron oxide[1] and possibly, by those of alumina present; closer consideration of the facts compels the rejection of this explanation; for the iron oxide and alumina constitute only about 36 and 60 per cent. respectively of the acid-soluble material, while Hilgard[2] found that they constitute about 42 and 52 per cent. respectively of the average acid-soluble material in 466 soils, chiefly of the Gulf States in which the tertiary formation occurs.

Nor can the extensive decomposition be attributed to solvent action upon such anhydrous silicates as chrysolite, leucite, labradorite, epidote, phlogopite or biotite, which are capable of complete or quite extensive decomposition by the hot acid employed; the quantities of alkalies and magnesia dissolved, are too small to account for any large percentage of such minerals.

One indicative feature of these soils is the large proportion of soluble silica they yield upon decomposition, ranging from 17.45 to 27.08 per cent. The limestone clay of Lancaster County has

[1] *Cf.* Grouven, Soils of Benkendorff, Prerau and Tillada, *Jahrb. Agr. Chem.*, **10**, 35.

[2] Bulletin 3, U. S. Weather Bureau, Division of Soils, p. 30.

been found to yield but 11.82 per cent;[1] Maxwell,[2] analyzing a composite sample representing twenty soils from the Northern United States, chiefly of the humid region, obtained only 7.284 per cent.; Hilgard[3] found, in 119 soils from Tennessee, Mississippi, Louisiana, Indian Teritory, and Texas, an average of 7.53 per cent., the accompanying insoluble matter being 74.74 per cent. Among the latter soils, however, thirteen show percentages of soluble silica ranging from 15.41 to 23.45 per cent., with accompanying insoluble matter, ranging from 34.8 to 53.19 per cent. The soluble silica in the Cuban soils is remarkable therefore for its large proportion to the entire soil, but not for exceptional quantity relative to the material decomposed by acid.

The large amount of water of hydration together with the ready decomposition of the soil under influence of hot acid, point to extensive weathering as the condition that has influenced the nature of the soil materials.

The results here observed may be due either to the slight resistance the original rock offered to weathering, to long exposure of more resistant rock, or to the separation of highly weathered material from that which has been less decomposed and its accumulation in the chalk beds from which these soils are derived.[4]

As instances of the first-class, the weathering of certain lavas may be cited. Maxwell[5] has found dark red, lava soils of Hawaii composed of readily decomposable hydrous silicates and iron oxide, the average of 120 analyses showing only 21.034 per cent. of resistant mineral matter, 16.168 per cent. of soluble silica, 17.499 per cent. loss upon ignition due chiefly to water of hydration, and 22.942 and 16.831 per cent. respectively of iron oxide and alumina soluble in acid. Hiola[6] and King[7] have reported analyses of tufa subsoils from Kumaba and Shimosa, Japan, that are marked by great loss upon ignition, high soluble

[1] Report Pennsylvania Experiment Station, 1894, p. 160.

[2] "Lava and Soils of the Hawaiian Islands," (1898), p. 101.

[3] X. Census, Vol. V.

[4] The tendency of lime to aid in forming zeolitic minerals from more resistant materials, can not be accepted in explanation of the observed ease of decomposition in these soils, because limestone clays in general are far more resistant to the action of acids.

[5] "Lavas and Soils of the Hawaiian Islands," (1898), p. 97.

[6] *Mitth. deutsch. Ges. Naturw. Volkerkunde Ostaneria*, 1881; *Jahbr. Agr. Chem.*, **24**, 25.

[7] *Jahbr. Agr. Chem.*, **24**, 22.

silica and very low acid-resistant substance, though in these soils, the alumina greatly exceeds the iron oxide. Not all volcanic soils show these characters, those of Sumatra and Java[1] being quite different.

The second hypothesis requires the parent rock to have been highly homogeneous and to have weathered under conditions that protect the weathered products from mechanical separation. The range in state of weathering exhibited by the several mineral materials of most sedimentary soils, raises grave doubt as to the occurrence anywhere of conditions that would permit the removal of calcareous materials, such as these soils have experienced, without the removal, at the same time, of the finer, more highly weathered siliceous materials from those less weathered.

On the other hand, very fine silt and clay representing the most highly weathered portions of rocks and soils separated mechanically from the coarser materials, show marked similarity in composition to these Cuban soils. Merrill[2] found the silts from decomposed granite, gneiss and diabase to be marked by high water of combination (8-14 per cent.), and of gelatinous silica (12-23 per cent.), with a resistant residue ranging from 59 per cent. in the case of granite to 16 per cent. in that of diabase; the acid-soluble alumina ranged from 9.2 to 24.9 per cent. and in each instance exceeded the iron oxide. Loughridge[3] found, in the 21.64 per cent. of clay separated by mechanical analysis from a certain soil, conditions very different from those in the entire soil:

	Clay. Per cent.	Entire soil. Per cent.
Loss upon ignition	9.00	3.14
Acid-resistant mineral matter	15.96	70.53
Gelatinous silica	33.10	12.30
Acid-soluble material	58.06	14.66
	100.14	100.63

It would seem from these data last cited, that very fine silt carried far out into the gulf and deposited where the foraminiferous skeletons that form the chalk were accumulating, would give rise to a soil of the properties noted in these Cuban soils.

[1] Van Bemmelen, *Op. cit.*, 257 and 393.

[2] "Rocks and Rock-Weathering, and Soils," (1897), pp. 212-220.

[3] Proceedings A. A. A. S., **22**, 81; Wiley: "Principles and Practice of Agricultural Analysis," Vol. I, p. 247.

These red soils are not of purely local occurrence. A. E. Woods[1] notes the prevalence in Bermuda of peculiarly deep red soils, whose color changes upon long cultivation. Earle[2] reports a partial analysis of a Cuban soil, of locality not stated, which exhibits high water of combination, low magnesia and alkalies, low acid-insoluble material (including gelatinous silica) but high calcium carbonate—a soil resembling those above reported except that it still retains much of the associated calcareous material. Watts[3] reports a red, limestone clay, tobacco soil from Mocho, Clarendon, Jamaica, that contains only 0.50 per cent. calcium carbonate, only 19 per cent. of acid-insoluble matter, including gelatinous silica, but which has 46 per cent. of iron and aluminum oxides and a large percentage of combined water.

While these soils may come under the Russian soil survey classification of laterites,[4] and like the true laterites of India possess deep red color, their large humus content differentiates them from the latter, from which they differ also in other respects.[5]

The peculiar violet-red color of these soils may be due to the dehydrating effect of salt water which W. Spring[6] and F. Katzer[7] have observed in case of uncombined ferric oxyhydrate deposited in delta-formations and upon sea-bottoms. Dr. Hayes, in the letter earlier mentioned, notes, however, that much of the soil apparently derived from the same formation in more easterly parts of Cuba, has a gray instead of red color. This difference may possibly be due to changes upon exposure of the virgin soil, such as Woods mentions as occurring in Bermuda.

The writer has found no record of any analysis of a soil of the Oligocene portion of the tertiary formation in the United States. Analyses of a few Eocene soils from the central prairie region of Mississippi reported by Hilgard[8] exhibit a very different composition.

[1] *Science*, June, 1902.

[2] Florida Experiment Station, Bulletin No. 19, p. 11.

[3] Journal Jamaica Agricultural Society, (1899), pp. 17-23; Experiment Station Record, No. 10, pp. 933-934.

[4] *Cf.* N. Sibirtzew, Mem. pres. au. Congres geol. Internat., St. Petersburg, 1897; *Jahrb. Agr. Chem.*, **42**, 66.

[5] *Cf.* J. W. Leather: Agr. Ledger, (1898), No. 2, p. 83; Experiment Station Record, **10**, 421.

[6] *N. Jahrb. Min.*, (1889), **1**, 47; *Jahrb. Agr. Chem.*, **42**, 49-50.

[7] Petermann's geog. Mitth., 1897; *Jahrb. Agr. Chem.*, **42**, 51.

[8] X. Census, Vol. V, p. 284.

MINERAL CHARACTER.

Attempts at separation into groups of minerals of different specific gravity by the use of Thoulet's solutions of 3.09 and 2.7 sp. gr., and at identification of the minerals present by microscopic means, were rendered abortive by reason of the flocculation of the fine particles and their deep coloration by iron. The use of hydrochloric acid to remove the iron was not attempted because of the readiness with which the silicates present, are decomposed. The separate groups obtained by mechanical analysis each contained from 57 to 60 per cent. of iron and aluminum oxides, so homogeneous were the flocculation aggregates.

The proportions of the several chemical constituents present throw a little light upon the possibilities of combination. The low solubility of the potash and phosphoric acid in 1 per cent. citric acid indicates that the former is chiefly combined with silica and the latter with iron oxide or alumina; its quantity corresponds to 1.16 to 1.45 per cent. of ferric orthophosphate. The carbonic acid is sufficient in most cases to combine with nearly all of the alkaline earths, and, in case of the San Antonio surface soil, also with most of the alkalies; the existence of a little ferrous carbonate seems probable; in like manner, the humus is probably sufficient to combine with most of the alkaline and earthy bases, so that the carbonic and humus acids must exist in partial combination with the iron; owing to the low combining power of the humus, it would not tie up any large proportion of the latter element.

No analytical data were obtained to establish the degree of oxidation of the iron present, but the deep red color points to a highly oxidized condition. No iron-containing silicates remain in the acid-resistant material, which is colorless.

Concerning the nature of the siliceous compounds present: No large part of the gelatinous silica can be derived from zeolitic combination, as the small quantities of alkalies and lime, and the very slight loss of water that occurs when the air-dried soil is heated at a temperature of 100° C. show.[1] Assuming that such zeolites are present as natrolite or phillipite, which require a minimum of lime, they could not make up more than 4.5 per cent. of the dry soil nor yield more than 0.70 per cent. of gelatinous silica.

[1] *Cf.* Hillebrand: Bulletin No. 176, U. S. Geol. Survey, p. 36.

Assuming that the iron is present as ferric oxide chiefly, the small quantities of gelatinous silica and alumina required for zeolitic combination may be disregarded and their ratios be directly considered to ascertain what evidence they offer as to their compounds present. The silica-alumina ratios in these soils range from 1.029 to 1.636, chiefly approximating the latter figure. The average ratio for the 119 southern soils analyzed by Hilgard[1] is 1:0.71; those for the common aluminous minerals decomposable by hydrochloric acid with a liberation of gelatinous silica, range from 1:0.42 to 1:0.85; allophane and chloritoid (ratios 1:1.71 and 1:1.46 respectively) are the most prominent exceptions, but its dark color and low hydration exclude the latter from playing any important part, while allophane has a too low specific gravity and too high hydration. Upon any of the hypotheses as to the combination of the bases other than alumina, the average specific gravity of these remaining minerals must lie between 2.2 and 2.5 and the water of hydration between 14.6 and 17.0 per cent.

Hilgard[2] found, in the Eocene soil of Mississippi earlier cited, a ratio of 1:1.34, approaching that of these Cuban soils, and noted in many southern clays an excess of alumina. He suggests the presence of gibbsite, a hydrated alumina, as a means of explaining both the composition and the cultural peculiarities of these lands. Assuming the presence of a decomposable aluminum silicate with a silica-alumina ratio and hydration like those of kaolinite, approximately one-half of the alumina of the Zorilla surface soil would be left to be accounted for; but the great hydration of gibbsite (34.5 per cent.) excludes it from acceptance as the source of the alumina.

Schloesing[3] has employed a dilute solution of sodium hydroxide in recent studies upon the condition of alumina in French and Madagascar soils; kaolin and fatty clay gave up to this solvent an excess of silica over alumina and continued to do so upon repeated treatment; on the other hand, a certain ochreous type of Madagascar soils yielded from 1 to 2 per cent. of silica and 8 to nearly 12 per cent. of alumina in the first treatment, but an excess

[1] *Op. cit. supra.*
[2] X. Census, Vol. V, pp. 67 and 284.
[3] *Compt. Rend.*, **132**, 1203; *Bied. Centrbl.*, **30**, 723-730.

of silica on repeated treatment; this he regards as indicating the presence of free alumina which is dissolved at once by the alkali. That soil was gravelly, however, and much of the alumina was extracted from the coarser materials separated by mechanical analysis; the land was fertile. Owing to lack of material, it has been impossible to apply this treatment to the Cuban soils; many other interesting observations have been omitted for the same reason. It is hoped that the peculiarities of these widely extended West Indian soils here reported, may lead others to more thoroughly study them.

A few words respecting the fertility of these Cuban soils: Their present content of calcium and magnesium carbonates is sufficient to keep them permeable, to provide for nitrification and to furnish all of these elements that may be needed to keep the soil sweet and the plants well fed. Magnesia is less abundant than lime, a condition very commonly reversed in the soils of the Gulf States. Potash is low but, owing to the presence of the lime, may not exhibit deficiency for some time. Phosphoric acid is unusually abundant, but of low availability because of its combination with iron or aluminum. These lands will, for this reason, as well as to insure continuance of permeability, require occasional calcareous manuring. Nitrogen is present in liberal supply.

[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION, NO. 9.]

THE EFFECTS OF FERMENTATION UPON THE COMPOSITION OF CIDER AND VINEGAR.

BY C. A. BROWNE, JR.

Received October 24, 1902.

THE present work comprises the results obtained in connection with an experiment begun at this Experiment Station in the Fall of 1898, which had for its object a chemical study of the cask methods of producing cider and vinegar, as ordinarily practiced in the rural sections of this country. So far as known, no experiments have been published thus far towards this end.[1]

PLAN OF THE EXPERIMENT.

The juice for the experiment was prepared wholly from one

[1] Reference should be made to Bulletin No. 127, of the Va. Agr. Expt. Station, by W. B. Alwood and R. J. Davidson, entitled "Observations on the Production of Vinegar in Cellars," which has since come to the writer's attention.

kind of apples of an unknown variety. The apples were picked November 15, 1898, and were taken at once to a cider mill near-by where they were ground and pressed. A 25-gallon cask was filled with juice and then taken immediately to a cool, dry cellar, where it was kept throughout the experiment. The bung of the cask was loosely drawn to allow the escape of carbon dioxide during fermentation. The first sample for analysis was drawn the day after pressing. Samples were then drawn about every two weeks during the early stages of the alcoholic fermentation; afterwards during the latter part of the alcoholic fermentation and throughout the acetic fermentation, when chemical changes advanced less rapidly, analyses were made only monthly or bimonthly.

In sampling, a quart jar was usually filled, the cider being drawn off through a rubber siphon from about the middle of the cask. Care was taken not to disturb the sediment which settled out during the fermentation. The temperature of the cellar and cider were taken at the time of sampling, and the cask containing the cider was weighed occasionally in order to ascertain the losses from evaporation and seepage. The samples after taking to the laboratory were also weighed before beginning the analysis, to determine the amounts removed from the cask. The samples were drawn always in the morning, and the analytical work was begun immediately after taking to the laboratory to avoid vitiation of results due to the progress of the fermentation. If turbid or containing matter in suspension, the samples were filtered before analyzing. The results of the analytical work, covering a period of over three years, are presented in Table I.

THE ALCOHOLIC FERMENTATION.

The determinations of solids in Table I were unfortunately all made by the old method of drying at 100° C. in a water-bath. A constancy in weight could never be secured, and the percentages given represent simply the solid matter after ten to twelve hours' drying. As compared with a method[1] used later upon fruit products of drying *in vacuo* at 70° C., this procedure gives too low results, owing to the decomposition of levulose.

Looking at the percentages of the sugars, sucrose, dextrose, and levulose, in Table I, we notice during the first two weeks a

[1] This Journal, **23**, 873.

TABLE I[1].—EFFECTS OF FERMENTATION UPON THE COMPOSITION OF CIDER AND VINEGAR.

	Date of analysis.	Temperature of cellar.	Temperature of cider.	Weight of sample.	Weight of cider in cask after sampling.	Specific gravity 17.5° C.	Solids at 100° C.	Ash.	Rotation, Ventzke, 400 mm. tube.	Levulose.	Dextrose.	Sucrose.	Total sugar after inversion.	Alcohol.	Volatile acid as acetic.	Fixed acid as malic.	Pectin.	Ester number.
		°F.	°F.		Grams.	Grams.	Per cent.	Per cent.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Alcoholic fermentation.	1898, Nov. 16	44	49	2004	95070	1.0577	13.75	0.26	—44.18	7.38	2.90	2.93	13.36	0.43	0.04	0.42	0.12	..
	1898, Nov. 30	50	46	1017	.....	1.0462	12.25	0.24	—53.78	7.29	2.86	1.20	11.43	1.67	0.05	0.43	...	..
	1898, Dec. 16	51	50	1000	.....	1.0331	9.48	0.24	—50.45	6.28	2.06	0.50	8.87	3.05	0.06	0.43	...	..
	1899, Jan. 5	60	58	1033	.....	1.0133	5.92	0.24	—29.60	2.88	1.21	0.09	4.19	5.32	0.08	0.40	...	..
	1899, Jan. 19	52	47	1050	.....	1.0067	4.53	0.24	—18.80	2.02	0.44	0.01	2.47	6.03	0.09	0.38	0.09	..
	1899, Feb. 2	34	35	1062	.....	1.0026	3.03	0.25	—13.00	1.41	0.29	0.00	1.70	6.49	0.10	0.31	...	..
	1899, Feb. 16	55	47	830	82440	1.0013	2.89	0.25	—11.06	1.17	0.21	...	1.38	6.70	0.11	0.30	...	5.8
	1899, March 9	50	49	1045	80850	0.9982	2.24	0.25	— 5.30	0.54	0.07	...	0.61	6.92	0.11	0.23	...	5.9
	1899, April 3	47	45	1038	79040	0.9968	2.10	0.25	— 3.40	0.30	0.00	...	0.30	6.93	0.17	0.21	...	9.0
	1899, May 4	72	64	1941	76770	0.9969	1.94	...	— 2.30	0.24	...	...	0.24	7.00	0.27	0.21	0.03	10.1
Acetic fermentation.	1899, July 27	67	62	1917	74960	0.9959	1.80	0.26	— 1.50	0.11	...	...	...	6.86	0.52	0.20	...	8.2
	1899, Aug. 14	68	66	1060	.....	0.9965	1.53	0.26	— 1.20	0.11	...	...	...	6.66	1.11	0.17	...	5.4
	1899, Oct. 2	55	50	1000	.....	0.9988	1.48	0.27	.....	...	...	...	...	6.01	1.77	...	...	..
	1899, Nov. 27	47	43	1079	.....	1.0017	1.42	0.26	.....	...	...	...	...	4.80	2.59	...	...	..
	1900, Feb. 14	54	46	1080	.....	1.0037	1.45	0.26	.....	...	...	...	...	4.54	3.67	...	...	..
	1900, April 20	65	58	1095	64980	1.0060	1.37	0.26	— 1.40	0.18	...	...	...	3.77	4.31	0.14	...	..
	1900, July 31	70	66	1090	63620	1.0113	1.70	0.25	— 1.20	0.22	...	...	...	2.61	5.98	...	...	..
Destructive fermentation.	1902, Feb. 10	..	..	....	44570	1.0162	2.40	0.48	— 5.00	1.20	...	...	...	0.00	3.33	0.06	...	..
	1902, March 9	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	3.12	...	...	..
	1902, April 7	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	2.76	...	...	..
	1902, May 19	..	..	....	.....	....	...	...	.....	...	...	...	...	...	2.25	...	...	..
	1902, June 16	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	1.98	...	...	..
	1902, July 22	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	1.28	...	...	..
	1902, Aug. 15	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	0.78	...	...	..
	1902, Oct. 13	..	..	....	.....	.....	...	...	.....	...	...	...	...	...	0.15	...	...	..

[1] All determinations, except that of solids, were made according to methods described in this Journal. **23**, 869 (1901).

rapid fall in the per cent. of sucrose, but that the percentages of dextrose and levulose remain nearly constant. This would indicate that in the beginning, by the action of the invertase upon the sucrose, the amounts of dextrose and levulose are restored nearly as fast as fermented. The following diagram will show the rates of decrease in the sugars, and their relations to alcohol and rotation more graphically.

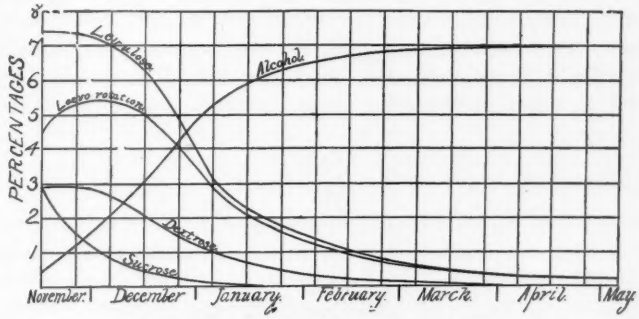


Diagram No. 1. Each division represents ten days.

The effect of the removal of the sucrose, which is strongly dextro-rotatory, is shown most strikingly by the marked rise at first in the levo-rotation; the maximum is soon reached, however, and the rotation then begins to fall, gradually at first,—the removal of sucrose and dextrose at this time very nearly counterbalancing the decrease in rotation that would be produced by the fermentation of levulose—, and then more suddenly owing to the increased rapidity in the fermentation of the levulose. The period of greatest chemical activity is from the fourth to the seventh week; we notice here the largest drop in the percentage of levulose, attended by the greatest rise in the percentage of alcohol. Another important fact is that while the sucrose and dextrose are completely removed by fermentation, a small amount of levulose remains unaffected. This is due to the formation of acetic acid, which arrests the alcoholic fermentation, as will be explained later. The levulose remains largely in excess of the dextrose during the whole fermentation, as is indicated by the marked levo-rotation at all times.

In plotting the curve for rotation one-tenth of the actual read-

ings given in Table I were used, in order to bring the curve within the range of the others. We note here that the rotation curve, as thus plotted, follows from its point of maximum the course of the levulose curve quite closely, gradually approaching the latter as the sucrose and dextrose diminish, until, with the elimination of these restraining factors the two curves merge, continuing afterwards together. The fact that the percentages of levulose, as calculated from the copper-reducing power, in the latter part of the alcoholic fermentation agreed so closely with one-tenth the observed polariscopic readings (Ventzke), in the 400 mm. tube, led the writer to calculate the theoretical Ventzke readings (20° C.) for a number of levulose solutions of different concentrations.

The formula[1] used was $v = \frac{4WP}{34.68}$, in which $v =$ the Ventzke reading sought, $W =$ grams of substance in 100 cc. solution, and $P =$ the specific rotatory power at 20° C. for the given concentration. In calculating the value of P for levulose, the formula of Jungfleisch and Grimbert[2] was employed, $[\alpha_D] = -[101.38 - 0.56t + 0.108(c - 10)]$, in which t is the temperature of the solution and c the grams of levulose in 100 cc.

TABLE II.

Concentration. Levulose in 100 cc. Grams.	Calculated specific rotatory power. 20° C.	Calculated polariscope reading, Ventzke, 400 mm. 20° C.
10	−90.18	−104.00
5	−89.64	− 51.69
2	−89.33	− 20.60
1	−89.21	− 10.26
0.5	−89.15	− 5.14
0.2	−89.12	− 2.06
0.1	−89.11	− 1.02

Thus, for quantities of levulose up to 2 grams per 100 cc., one-tenth of the polariscopic reading in the 400 mm. tube at 20° C., gives a result agreeing within a few hundredths of the amount of levulose actually taken. This fact seems to offer a ready and easy means of determining levulose in the absence of other sugars. For low concentrations of levulose the differences between grams in 100 cc. and actual percentages are negligible. The close agree-

[1] This Journal, **23**, 881.

[2] Landolt: "Das optische Drehungsvermögen," 2 Auflage, p. 524.

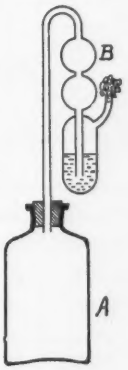
ment between the above calculated results and those actually observed in Table I affords not only a check upon the work, but also an indication that levulose is the only important optically active body in completely fermented ciders.

As regards other chemical changes produced during the period of alcoholic fermentation, we observe a slow, but gradual increase in the percentage of acetic acid, while as regards the percentage of fixed or malic acid, the reverse is true. Just how the malic acid is destroyed is not well understood. A similar diminution takes place with tartaric acid in the fermentation of grape juice. The amount of pectin or gummy matter precipitated by alcohol was determined in a few cases during the alcoholic fermentation, and also seems to undergo a decrease, due no doubt to sedimentation.

Determinations of the ester number, or cubic centimeters of N/10 sodium hydroxide necessary to saponify the esters distilled from 100 cc. of cider were made in the latter part of the period of alcoholic fermentation. The results seem to indicate an increase in the volatile esters up to the point of greatest alcohol content; with the development of acidity, however, as shown by later analyses, these esters seem to be partly broken up. The maximum ester number of 10.1 would be equivalent to 0.09 per cent. of ethyl acetate.

THE SUGAR-ALCOHOL RATIO.

Kulisch[1] in an experiment upon the fermentation of apple juice calculates that 100 parts of sugar after inversion yield 49.5 parts of alcohol, but does not state whether the experiment was conducted in a cask or bottle.[2] The results of Kulisch are based



[1] Kulisch: *Landw. Jahrb.* **19**, 111, (1890).

[2] Larger yields of the alcohol are, of course, obtained where fermentation bottles are used since losses from evaporation are prevented. In some fermentation experiments carried out by the writer under the direction of Professor Alfred Koch, at the University of Göttingen, there were obtained in one experiment from 100 parts of sugar, 50.49 parts alcohol and 48 22 parts carbon dioxide. Sterilized grape juice and a pure yeast culture (Reinhefe No. 13) were employed, so that all injurious fermentative changes, acetic, etc., were excluded. The fermentations were carried out in flasks of the form shown in the accompanying figure. After sterilizing the apparatus the bottle *A*, holding about 500 cc., is filled about half full with a known quantity of the sterilized medium (must, cider, wine, etc.) and then, after inoculating, tightly closed with the ar-

upon the supposition that the volume of liquid remains constant throughout the fermentation; while this assumption is practically correct as is shown by the results of Stein[1] and others, it would not hold where there were losses from evaporation and seepage, as is always the case where the fermentation takes place in casks.

To determine the yield of alcohol from sugar in the experiment, the calculation was made as follows, using the data given in Table I.

Date.	Weight of cider. Grams.	Sugar in cider. Per cent.	Sugar in cider. Grams.	Alcohol in cider. Per cent.	Alcohol in cider. Grams.
Nov. 16	97070	13.36	12968.6	0.43	417.4
May 4	76770	0.24	184.2	7.00	5373.9

12968.6 grams = total weight of sugar at beginning of fermentation.
deduct 184.2 " = " " " " " end " "

12784.4
deduct 585.6 grams = total weight of sugar removed by samples.

12198.8 grams = weight of sugar actually fermented.
5373.9 grams = total weight of alcohol at end of fermentation.
deduct 417.4 " = " " " " " beginning of fermentation.

4956.5
add 579.0 grams = total weight of alcohol removed by samples.

5535.5 grams = weight of alcohol formed during period of fermentation.

$$\frac{5535.5}{12198.8} = 0.454, \text{ sugar-alcohol ratio.}$$

In other words 100 parts of sugar in the experiment gave an actual yield of 45.4 parts alcohol. This is 88.8 per cent. of the theoretical yield and about 90 per cent. of the best results of laboratory experiments.

The principal cause of this loss in alcohol is that from volatilization. A small laboratory experiment upon the effects of evaporation, at room temperature, on a dilute alcohol solution showed the following:

	Weight of solution. Grams.	Specific gravity. 15.5° C.	Alcohol. Per cent.	Alcohol in solution. Grams.
At beginning	188.5	0.98647	8.11	15.29
After forty-eight hours ..	142.2	0.99802	1.04	1.48
Loss	46.3	.....	....	13.81

rangement *B*. The bottom bulb is filled about half full with sulphuric acid (1:1), which seals the flask from without, but does not interfere with the escape of carbon dioxide. The mouth of the bulb is closed with a small wad of cotton. By weighing the apparatus from time to time and noting the loss in weight, one is enabled to follow the rate of fermentation very closely.

[1] *J. Soc. Chem. Ind.*, **19**, 127–8 (1900).

Thus 30 per cent. of the loss on evaporation was due to alcohol, while of the total amount of alcohol originally present 90 per cent. disappeared by volatilization at room temperature. This illustration is, of course, an extreme case; the experiment was conducted in an open beaker and a relatively large surface (10 square inches) was exposed to evaporation in proportion to the amount of solution.

The loss from evaporation in the cider experiment during the 169 days of the alcoholic fermentation was calculated as follows:

	97070 grams	= weight of cider at the beginning.
deduct	76770 grams	= weight of cider at the end of the alcoholic fermentation.
	20300	
deduct	12020 grams	= weight of cider removed by samples.
	8280 grams	= loss from evaporation and carbon dioxide.
deduct	5964 grams	= theoretical weight of carbon dioxide by fermentation of 12198 8 grams sugar.
	2316 grams	= the calculated loss from evaporation and seepage.

The outer surface of the cider cask showed no signs of leakage, so that the greater part of this loss, which amounts to about 2.4 per cent. of the total amount of liquor, was probably due to evaporation,—this being increased no doubt by the abundant evolution of carbon dioxide early in the fermentation. In this loss from evaporation a considerable quantity of alcohol must have escaped.

Very serious losses of alcohol may result in cider-making, from the development of the acetic ferment. During the period of alcoholic fermentation in the experiment, there was formed 0.23 per cent. acetic acid, equivalent to about 0.2 per cent. alcohol; and sufficient to cause a decrease of 0.7 in the percentage of alcohol formed from sugar.

The average percentage of acetic acid in a number of ciders, obtained from farmers and analyzed at this station, was found to be 0.69, the results ranging from 0.24 to 1.96 per cent. Kulisch[1] found in the analysis of many German ciders an average of only 0.04 per cent. acetic acid, the range being from 0.01 to 0.14 per cent. This low degree of acidity is especially noteworthy and is an indication of the extreme care employed in the fermentation.

[1] Kulisch: *Landw. Jahrb.*, **19**, 88 (1890).

By racking ciders off after the main fermentation into other casks and bunging tightly, a considerable part of the losses of alcohol from evaporation and acetification may be prevented, and a much better quality of cider obtained.

THE ACETIC FERMENTATION.

The cider obtained by the alcohol experiment was used for the experiment on acetification. The cider was not transferred; but to facilitate the process of oxidation the bung of the cask, which had been only loosely inserted during the alcoholic fermentation, was now removed entirely. The results of the analytical work are tabulated in the second part of Table I. The writer, owing to a temporary absence of eighteen months, was unable to carry the experiment through to the completion of acetification. The last analysis shows the presence of 2.61 per cent. alcohol and this would correspond to about 3 per cent. more acetic acid, so that the vinegar at the end of acetification showed probably about 9 per cent. acetic acid. The work was, however, carried far enough to illustrate the principal chemical changes of acetification and to establish an alcohol-acetic acid ratio.

Inspecting Table I we notice that with the progress of acetification the specific gravity, which had been steadily decreasing since the beginning of the alcohol fermentation, now begins to increase. The percentage of solids determined by drying at 100° C. undergoes a slight diminution; the last analysis, however, seems to show an increase, due, perhaps, to a concentration of the liquid from evaporation. Ash remains constant. The percentage of malic or fixed acid continues to decrease, as during the alcoholic fermentation. The percentage of levulose continues to decrease at first slightly,—the result of the last remaining efforts of the alcoholic ferment,—but upon the percentage of acetic acid reaching 0.5 undergoes no further diminution. The alcoholic fermentation proceeds best in the presence of a minimum amount of acetic acid. A percentage of 0.5 acetic acid will retard the alcoholic fermentation considerably, and experiments by Lafar[1] show that out of fifteen different varieties of yeasts only three were able to produce any fermentation at all when the

[1] Lafar: *Landw. Jahrb.*, **24**, 445 (1895).

amount of acetic acid exceeded 1 per cent. Many farmers and vinegar manufacturers make a foolish practice of adding fresh apple-juice to old vinegar stock, in the hope of thus securing a more rapid conversion of the product into vinegar and then complain that their vinegar "won't make." The sugar of the juice must first undergo the alcoholic fermentation before the acetic fermentation can begin, and by adding apple-juice to old vinegar, the alcoholic fermentation may not only be checked, but even absolutely prevented. The writer knows of instances where such mixtures have remained for years without fermenting. This fact no doubt explains the high percentage of reducing sugars found occasionally in samples of cider vinegar.

The relation between alcohol and acetic acid in the fermentation experiment is illustrated graphically in the following diagram.

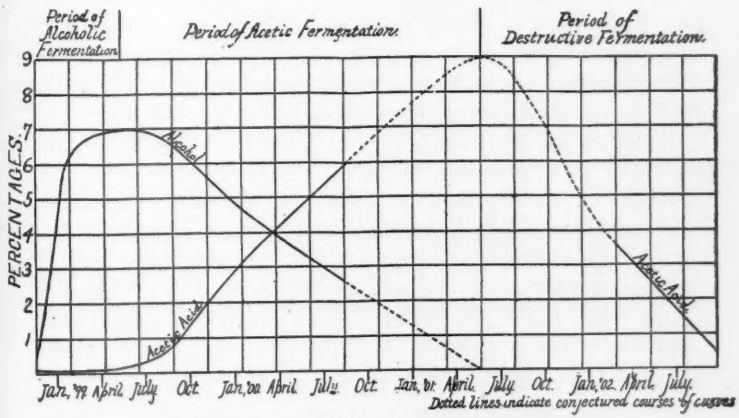


Diagram No. 2. Each division represents ten weeks.

The process of acetification advances very slowly until about July when it receives a sudden start, probably through the influence of the warm summer temperature. The conjectured courses of the alcohol and acetic acid curves, for the time when no analyses were made, are indicated by dotted lines.

THE ALCOHOL-ACETIC ACID RATIO.

Calculations made from the specific-gravity tables of alcohol and acetic acid, indicate that there is a slight increase in volume

during the acetic fermentation, provided no loss occurs from evaporation. Assuming that the volume remains unchanged during the fermentation, a calculation of the ratio of alcohol to acetic acid, from the data in Table I, gives a value of 1.33, which instead of being lower is higher than the theoretical figure 1.30. This is to be explained by a concentration of the acetic acid, during the experiment, from evaporation. A laboratory experiment[1] upon the effects of evaporation on a dilute solution of acetic acid at room temperature showed the same effect.

	Weight of solution. Grams.	Specific gravity. 15.5° C.	Acetic acid by titration. Per cent.	Acetic acid in solution. Grams.
At beginning.....	188.5	1.01184	8.53	16.08
After forty-eight hours ..	155.5	1.01326	9.04	14.06
Loss	33.0	.....	....	2.02

This shows a concentration of the solution from evaporation, there being an increase of 0.5 per cent. acetic acid in forty-eight hours. A calculation, based upon the actual amounts of acetic acid in the solution, shows, however, a loss of 2.02 grams acetic acid from evaporation or 12.5 per cent of the original amount. Vinegars may, therefore, become stronger through evaporation, notwithstanding that there is an actual loss of acetic acid.

To determine the true ratio of alcohol to acetic acid in the experiment, the following calculation was made, using data from Table I.

Date.	Weight of vinegar.	Alcohol in vinegar. Per cent.	Alcohol in vinegar. Grams.	Acetic acid in vinegar. Per cent.	Acetic acid in vinegar. Grams.
1899, May 4	76770	7.00	5373.9	0.27	207.3
1900, July 31	63620	2.61	1660.5	5.98	3804.5

5373.9 grams = total weight of alcohol at beginning of experiment.
deduct 1660.5 " = " " " " " " end of experiment.

3713.4
deduct 432.8 grams = weight of alcohol removed by samples.

3280.6 " = " " " actually fermented.
3804.5 grams = total weight of acetic acid at end of experiment.
deduct 207.3 " = " " " " " " beginning of experiment.

3597.2
add 219.4 grams = weight of acetic acid removed by samples.

3816.6 " = " " " " formed during period of experiment.

$$\frac{3816.6}{3280.6} = 1.163, \text{ ratio of alcohol to acetic acid.}$$

[1] This experiment was conducted at the same time and under similar conditions as the experiment upon evaporation of alcohol in dilute solution, page 22.

In other words 100 parts of alcohol in the experiment gave an actual yield of 116.3 parts acetic acid, instead of 133.2 parts as calculated according to constant volumes. This yield is 89.2 per cent. of the theoretical. The greater part of this loss occurred no doubt from volatilization of both alcohol and acetic acid. In the experiment during the period of acetification the bung was withdrawn from the cask entirely, and considerable loss from evaporation might easily take place.

The loss from evaporation during the fifteen months of the acetification experiment was computed as follows.

76770 grams = weight of vinegar at beginning of experiment.
deduct 63620 grams = weight of vinegar at end of experiment.

13150 grams.
deduct 8321 grams = weight of vinegar removed by sample.

4829 grams.
add 2296 grams = calculated weight of oxygen absorbed to oxidize [3280.6 grams alcohol.

7125 grams = calculated loss from evaporation and seepage.

This loss or shrinkage is over 9 per cent. of the weight of cider at the end of the alcoholic fermentation, and if calculated to the completion of acetification would equal nearly 15 per cent.

Another source of loss of acetic acid, in addition to that from volatilization, occurs as a result of certain destructive fermentative changes. This will be spoken of more fully under the subject of deterioration of vinegar. The ratio of sugar to acetic acid in the experiment would be equal to the product of the sugar-alcohol and alcohol-acetic acid ratios, $0.454 \times 1.163 = 0.528$. That is, 100 parts of sugar produced 52.8 parts acetic acid, which is about 80 per cent. of the theoretical yield 66.6.

THE DETERIORATION OF VINEGAR.

It is a fact well known among vinegar manufacturers that vinegars after long standing deteriorate and lose their strength. Such vinegars they say become "overaged."

A good example of a deteriorated vinegar is afforded in the fermentation experiment. After an interval of eighteen months from the analysis on July 31, 1900, an examination of the vinegar was made with the results shown at the bottom of Table I. The vinegar, when drawn, contained a large amount of sediment,

mixed with mother and had to be filtered. There were also present many dead larvae of vinegar flies (*Drosophila*); whether these may have played any important part in the process of deterioration is uncertain.

Comparing the analytical results of the deteriorated vinegar with those of eighteen months before, we notice some very decided changes. The solids and ash have both undergone a marked increase, due to a concentration of the vinegar from evaporation. The bung-hole of the vinegar cask had remained open since the time of the former analysis and the weight of vinegar had decreased from 63 to 44 kilos, a loss of over 30 per cent. We note also in Table I that the alcohol has entirely disappeared in the deteriorated vinegar, as was to be expected, and that the percentage of malic acid, which had been decreasing from the very first, has fallen off to 0.06 per cent.

The acetic acid, it is noticed, has decreased over 2.5 per cent. since the last determination. The loss in acetic acid from deterioration is, however, much greater than this, as the process of acetification at the time of the former analysis was incomplete. Determinations of acidity in the deteriorated vinegar were made from month to month, and the decrease continued quite regularly, though somewhat faster in the summer months, at the rate of about 0.1 per cent. per week. This is also shown graphically in diagram No 2.

This marked decrease in the percentage of acetic acid is due mostly to a destructive fermentation. There are a number of acetic acid-consuming organisms, but of first importance among these are the acetifying bacteria themselves. It was first established by Pasteur that the acetic acid bacteria, after converting the alcohol into acetic acid, then consume the latter, forming carbon dioxide and water, $CH_3COOH + 4O = 2H_2O + CO_2$. The saying sometimes heard that vinegar on long standing "eats itself up" is therefore really true. This secondary action of the acetic ferment sets in no doubt before the complete acetification of the alcohol, and this would diminish somewhat the yield of acetic acid from alcohol.

THE NATURE OF THE ORGANISMS PRODUCING DETERIORATION.

A sample of the deteriorated vinegar poured off into a large

bottle continued to develop mother in large quantities, and the question arose as to the exact nature of the ferment producing the deterioration. A chemical examination of the mother, which was taken before the period of deterioration and of that found in the degenerated sample, showed that the organisms, which had produced acetification, and those causing the deterioration were of an entirely different nature, although both belonged to the class of acetic bacteria. Pieces of the mother from the deteriorated vinegar were boiled with successive portions of dilute sulphuric acid and soda, to remove incrusting substances, and then, after washing, treated with chloride of zinc and iodine; an intense blue coloration developed, characteristic of cellulose. The same reaction was also produced with sulphuric acid and iodine. This proves the ferment to be not the ordinary *mycoderma aceti* but *bacterium xylinum*[1] or an allied form,—the slimy envelopes of *mycoderma aceti* or *bacterium Pasteurianum* not containing cellulose. The presence of a cellulose-forming organism in the deteriorated vinegar is especially noteworthy, inasmuch as the mother taken from the vinegar before deterioration gave no cellulose reaction, showing that the ferment, which produced acetification, was of the ordinary *mycoderma* type. Bertrand[2] states that the small red vinegar flies (*Drosophila cellaris*), which frequent places where fruit juices, etc., are fermenting, inoculate the latter with the sorbose bacterium[3] (*bacterium xylinum*). As was before stated many larvae of vinegar flies were found in the deteriorated vinegar and we may have here a source of the organisms, which seem to have supplanted the original acetifying bacteria.

THE FORMATION OF REDUCING SUBSTANCES IN "OVERAGED" VINEGAR.

A singular fact in connection with the results upon deterioration is the high increase in the percentage of reducing sugar, which is also attended by a considerable increase in the levorotation. This cannot be explained altogether by the concentration of the vinegar from evaporation, since with a reduction in volume of only 30 per

[1] Lafar: *Technische Mykologie*, Bd. I, p. 346. The *Bacterium xylinum*, first studied by A. J. Brown, forms a very tough, thick mother, popularly designated in England as "vinegar plant."

[2] Bertrand: *Compt. Rend.*, **122**, 900; Maquenne: "Les Sucres," Paris, (1900), p. 581.

[3] The Sorbose bacterium and *Bacterium xylinum*, at first considered different, have been proved by Emerling to be identical. *Ber. d. chem. Ges.*, **32**, 541.

cent., we observe that the percentage of sugar, calculated as levulose, has increased to over five times its original amount. The percentage of sugar as levulose no longer agrees with one-tenth the rotation Ventzke in the 400 mm. tube, as was the case early in the process of acetification, but is over twice the same, so that other reducing substances besides levulose must be present,—the result no doubt of certain fermentative changes. This latter assumption does not seem improbable, when we consider the fact that the solids of vinegar are made up to a great extent of glycerol, pectin, and other substances, probably of a carbohydrate nature, and hence easily subject to chemical transformation.

To ascertain more fully the nature of the reducing bodies in the deteriorated vinegar, a quantity of the sample, after filtering from the mother, was treated with a solution of phenylhydrazine dissolved in acetic acid. After heating for twenty minutes on the steam-bath, a flocculent precipitate began to form and, on cooling, a thick yellowish colored magma was obtained. This was filtered off, and by fractional crystallization from alcohol was found to contain two well-defined osazones.

Osazone No. 1, present in considerable amounts, was easily soluble in alcohol, but less soluble in water. After recrystallizing several times from dilute alcohol, a yellowish colored product was obtained melting at 142°-143°. The compound turned slightly brown on long exposure to the air and light.

Osazone No. 2, present in only small amounts, was almost insoluble in alcohol and very difficultly soluble in ether. Its quantity was so small that no attempt was made to recrystallize it. It was purified by washing with small amounts of alcohol and ether. The compound consisted of a pale yellow crystalline powder, melting at 240°-242°.

An elementary analysis of osazone No. 1 showed it to have the composition of a phenyl hexosazone.

	Found. Osazone No. 1. Per cent.	Calculated. Phenylhexosazone, $C_{18}H_{22}N_4O_4$. Per cent.
Carbon	60.45	60.27
Hydrogen	6.22	6.20

Of the some twelve known isomeric phenylhexosazones only one has a melting-point agreeing with that of osazone No. 1 and

that is the phenylformosazone, described by Fischer,[1] melting at 144°. Formose,[2] a body of great interest in the synthesis of sugars, has not been found hitherto in any natural product. It has been prepared synthetically by the condensation of formaldehyde in alkaline solution. In this condensation a mixture of substances is formed, but the name formose is applied by Fischer only to the compound giving the above osazone. The arrangement in composition and melting-point of osazone No. 1 with phenylformosazone, while not an absolute proof of the identity of the two compounds, yet furnishes an indication of the presence in the deteriorated vinegar either of formose or of some unknown hexose sugar.

An elementary analysis of osazone No. 2 showed that it was not an osazone of any of the sugars. Its composition agrees, however, with that of phenyldiacetylosazone.

	Found. Osazone No. 2. Per cent.	Calculated. Phenyldiacetylosazone, $C_{16}H_{18}N_4$. Per cent.
Carbon	71.90	72.10
Hydrogen.....	7.08	6.82

Diacetylosazone, first prepared by Pechmann,[3] is described as a yellowish colored, finely crystalline compound, melting at 245°, almost insoluble in alcohol or water, and difficultly soluble in ether. These properties agree exactly with those of osazone No. 2. This osazone can be formed either from diacetyl, $CH_3COCOCH_3$, or from dimethyl ketol, CH_3—CHOH—CO—CH_3. The latter compound benig a ketone, alcohol is closely allied to the sugars and, as described by Pechmann,[4] reduces Fehling's solution strongly, even in the cold.

The separation of the two osazones just described from the deteriorated vinegar goes to confirm, what was previously surmised from the changes in reducing power and rotation, *viz.*, that other reducing substances besides levulose must be present as a consequence of fermentative changes. As a matter of fact, the levulose seems to have disappeared completely, since no traces of other osazones besides the two mentioned could be found.

As a remedy against deterioration, vinegars intended for storage should be racked off into clean casks, the latter filled full

[1] Fischer: *Ber. d. chem. Ges.*, **21**, 989–991.

[2] See Tollens: "Die Kohlenhydrate," Bd. II, p. 39 and p. 135; also Maquenne: "Le Sucres," p. 398.

[3] Pechmann: *Ber. d. chem. Ges.*, **21**, 2754.

[4] Pechmann: *Ibid.*, **22**, 2214.

and tightly bunged. Since none of the acetic organisms can thrive without air, their further development is thus prevented, and the loss from destructive fermentation reduced to a minimum.

MISCELLANEOUS RESULTS.

In the following tables a few miscellaneous results are given, which may have a certain interest, though not bearing directly upon the main part of the fermentation experiment.

The Composition of Vinegar Settlings. During the alcoholic and acetic fermentation a large quantity of matter settles to the bottom of the cask. A quantity of this material, as obtained from the cask at the close of the fermentation experiment, was filtered off, washed, and submitted to an examination.

The material, which was of a brownish color, was seen under the microscope to consist largely of dead yeast cells; fragments of mother, particles of pomace, and amorphous flocks of a pectinous character were also observed. In addition to these was noted a number of spherical bodies, more or less marked with a linear depression, which were stained blue with iodine. Measurements showed these to range in size from 0.004 mm. to 0.016 mm., which thus identifies them with the starch granules of the apple.[1] This starch, which was removed from the apple at the time of pressing the cider, settles out and remains unaffected by the fermentation.

An analysis of the dried settlings showed them to have the following composition:

TABLE III.

	Per cent.
Moisture	4.91
Fat	1.69
Protein	20.13
Ash	2.65
Crude fiber	5.69
Nitrogen-free extract	64.93

A determination of pentosans showed only 1.48 per cent., so that the high percentage of nitrogen-free extract remains unaccounted for. The amounts of starch and pectin present were not determined, and these no doubt would make up a considerable part of the deficiency.

Composition of Ash.—Analyses were made of the ash from the apples and cider used for the fermentation experiment and of the ash from the settlings, taken from the cask after closing the experiment.

[1] Bulletin No. 58, Pennsylvania Department of Agriculture, p. 12.

TABLE IV.

	Ash of apples. Per cent.	Ash of cider. Per cent.	Ash of settlings. Per cent.
K_2O	58.31	60.60	19.94
Fe_2O_3 and Al_2O_3	12.26	6.00	19.97
CaO	undetermined.	1.15	4.17
MgO	undetermined.	undetermined.	2.22
P_2O_5	12.51	7.12	29.64
SO_3	6.87	4.15	0.14
SiO_2	1.65	1.90	24.23
Undetermined CO_2, etc	8.40	19.08	....

The high percentage of silica and phosphoric acid in the ash of the settlings is noteworthy; no carbonates were present.

In concluding, the writer expresses acknowledgment to Messrs. C. P. Beistle and A. N. Diehl, former assistants at this experiment station, for help in much of the analytical work of the foregoing experiments, and also to Dr. William Frear for his encouragement and many kindly suggestions, and under whose initiative the work was first begun. The writer owes an especial debt of gratitude to his former teacher, Professor Alfred Koch, of Göttingen University, for much valuable advice and information upon this subject of fermentation.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS.]

A CONTRIBUTION TO THE CHEMISTRY OF FATIGUE.

BY HENRY WINSTON HARPER AND MARGARET HOLLIDAY.

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INTRODUCTION.

SOME years since, while engaged in the study of the phenomena of fatigue and breathlessness, the senior author of this contribution was struck with an apparent resemblance to the phenomena encountered when caffeïne is administered in toxic doses. It seemed clear that the phenomena of fatigue were largely due to the action of a chemical substance present in toxic quantity in the blood-stream, and that this substance had its origin in the muscles, *i. e.*, that the metabolism within the muscles undergoing excessive exercise was accompanied with a production of incompletely

oxidized chemical complexes, that these complexes possessed toxic qualities, and, transported by the blood-stream throughout the body, gave rise to the phenomena grouped under fatigue. Fatigue then arises from autointoxication, but the toxic substances are not the simple end-products, urea, carbon dioxide, etc., but are far more complex bodies, among which may possibly be found one or more of the alkyl derivatives of xanthine. A preliminary investigation pointed to the presence of methyl derivatives of xanthine, and encouraged further prosecution of the inquiry; but multitudinous duties stopped the work before fruitful results were obtained. The research was not again entered upon until during the session of 1901-1902, when the present investigation was undertaken in conjunction with Miss Margaret Holliday.

It should be distinctly understood that the results here presented are not offered as a solution of the problem of fatigue, but the data thus far accumulated are of sufficient interest to justify publication, and they represent at least a modest contribution to the chemistry of the subject. The main problem will be further investigated.

Lombard[1] states that: "The working cell liberates energy at the expense of its store of nutriment and oxygen, and through oxidation processes forms waste-products which are poisonous to its protoplasm. The fatigue which results from functional activity has, therefore, a twofold cause, the decrease in energy-holding compounds available for work and the accumulation of poisonous waste-matters." A similar statement is made by other physiologists; but it will be seen that such statements are only broad generalizations, and when specific information concerning the nature of the waste-products and the chemistry of their formation and action is sought, it then becomes apparent that a very large field for chemical research needs to be more deeply explored. It is equally clear that this field of investigation is full of difficulties, and, therefore, presents opportunities for numerous investigators. Like all biochemical problems, it includes a large amount of virgin soil.

The main object of this particular research was to shed some light upon the chemical nature of the metabolites which gain access to the blood-current during excessive muscular exertion.

[1] Lombard: "An American Text-Book of Physiology," 1901, Vol. II, p. 70.

It was not expected that anything approaching a solution of the problem would be speedily gained, but a hope of progress was entertained, and a definite plan of work for the future has been evolved. The question of the production of the methyl derivatives of xanthine within the muscles at the time of excessive muscular exertion and their discharge into the blood-stream was especially investigated, and every precaution was taken to exclude the access of these bodies through extraneous sources. The results are presented upon their own merits. A fuller discussion will accompany a later investigation.

ANALYTICAL METHODS USED.

A great deal of time was devoted to the calibration of apparatus, and to the trial of the numerous analytical methods used in biochemical work with a view to ascertain the limits of accuracy and suitability for this particular inquiry. The usual numerous disappointments were encountered; and some of the methods finally adopted are far from being wholly satisfactory. Some of the tabulated results well illustrate this statement of fact. In some instances results obtained by two or more entirely different methods are recorded.

The methods of analysis adopted by the Association of Official Agricultural Chemists[1] were used for the analysis of food-stuffs. Total nitrogen of the urine and of the feces, the nitrogen in the phosphotungstic acid precipitate, in the xanthine silver precipitate, theobromin silver precipitate, and purine copper precipitate, was determined by the Kjeldahl-Gunning method; the nitrogen as urea was determined by the method of A. Braunstein,[2] and also by the well-known sodium hypobromite method, and the filtrate from the phosphotungstic acid precipitate was similarly treated; nitrogen as ammonia was determined by the method of O. Folin;[3] the nitrogen as uric acid by the method of E. H. Bartley;[4] the phosphates were determined by titration with a standardized solution of a uranium salt; sulphates were determined gravimetrically as barium sulphate, following the method of O. Folin;[5] the

[1] Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, "Methods of Analysis."

[2] A. Braunstein: *The Analyst*, **26**, No. 304, p. 192.

[3] Otto Folin: *Ibid.*, **27**, No. 310, p. 20.

[4] E. H. Bartley: This Journal, **19**, 649.

[5] Otto Folin: *Am. Journal of Physiology*, **7**, 152.

chlorine was determined by Volhard's method. In the preliminary experiments with the phosphotungstic acid solution, it was found that the separation of caffeïne, from mixed solutions of urea, uric acid, hippuric acid and caffeïne, was more easily and completely effected when hydrochloric acid was used in place of sulphuric acid; accordingly, the phosphotungstic acid precipitate in which the nitrogen was quantitatively determined was obtained by this method. The urine (acidified with hydrochloric acid and the precipitant were both brought to the boiling-point and thoroughly mixed; and the filtration and washing of the precipitate was carried out with a hot-water funnel. The methyl derivatives of xanthine were sought by two methods: (1) that of Martin Krüger;[1] (2) that of H. W. Harper: a measured quantity of urine is evaporated to dryness on a water-bath and the residue is extracted with successive portions of hot purified chloroform; this solution is treated with animal charcoal, filtered hot and the dissolved salts obtained by fractional crystallization. In one of the precipitates obtained by the method of Krüger the nitrogen was determined by the absolute method. Particular pains were taken to obtain and use nitrogen-free reagents, and the Kjeldahl-Gunning determinations were carried out, as usual, with the parallel blank. The determinations were mostly made in duplicate and triplicate. The specific gravity was taken with a pycnometer. The calculations are on the basis of O = 16 (International Table of Atomic Weights, 1902).

EXPERIMENTAL PART.

Mr. M. B. W., a senior student in the University of Texas, was selected for the experiment. He was twenty years of age, five feet and eleven inches high, weighing 134.5 pounds, and of exemplary habits. He had never used coffee, tea, tobacco, or alcoholic liquors, nor had he tasted chocolate in six months. Throughout the period of the experiment it was not possible for any of the methyl derivatives of xanthine to gain access to his system from without.

The experiment began at 8 A.M., Sunday, May 11th, and ended at 8 A.M., Tuesday, May 20th, continuing nine days.

The diet was planned to keep the subject in nitrogen equilib-

[1] Martin Krüger: *Ber. d. chem. Ges.*, **32**, 2821.

rium. It contained whole milk, butter, bread, eggs, Malta-vita, sugar, lemons, and now and then a banana. An accurate account was kept of the weight of the foodstuffs consumed, and each day samples of the milk and bread were taken and the nitrogen of the same determined. The nitrogen in the Malta-vita and that in the butter was likewise determined, while that in the eggs, lemons and bananas was calculated from values given in Bulletin No. 28 (revised edition)—"The Chemical Composition of American Food Materials."[1]

The experiment was divided into three periods of three days each—a period of rest, a period of excessive exercise, a second period of rest. Throughout the periods of rest the subject confined himself to the performance of his usual routine college duties. During the middle period, in addition to his usual routine, he was required each day for three days to indulge in a hurdle race until he fell exhausted.

The urine was collected in clean tared bottles, retained in a refrigerator until the output of twenty-four hours was voided, then weighed, thoroughly mixed and analyzed.

The feces corresponding to the food eaten during each of the three periods were separated in the usual manner by means of willow charcoal. Four capsules were taken with the supper of May 10th; four capsules with the breakfast of May 14th; four capsules with the supper of May 16th; and four capsules with the breakfast of May 20th. The feces between the first and second charcoal represented the first period; that including the second and third charcoal marked the second period; and that between the third and fourth charcoal marked the third period. The feces were weighed, dried at 60° C., again weighed and analyzed.

Because of a misunderstanding, the pulse and temperature were not recorded during the first two days of the experiment. The observations subsequently made are recorded below.

The letters A, B, C, D, E, F, G, H, I represent successive periods of twenty-four hours each; A, B, C represent the first period of rest, D, E, F, the middle period (period of overexertion), G, H, I, the last period (second period of rest).

The following tables include the more important results of the experiment.

[1] "The Chemical Composition of American Food Materials," Bulletin No. 28, revised edition, U. S. Department of Agriculture, Office of Experiment Stations.

TABLE I.—PULSE AND TEMPERATURE DURING THE EXPERIMENT.

		Before exercise.			After exercise.					
Date.	Time.	Pulse.	Temperature. °F.	Time.	Weight.	Pulse.	Temperature. °F.	Weight.	Pulse.	Temperature. °F.
C 13	7.25 A.M.	64	97.4	.....	134.5	...	...	.....	...	...
	10.00 P.M.	60	97.2	.....	....	...	...	.....	...	...
D 14	7.25 A.M.	62	97.4	11.00 A.M.	134.5	106	98.8	134.25	202	98.0
	10.15 P.M.	60	97.2	12.00 M.	....	...	...	.....	90	99.3
E 15	7.25 A.M.	60	97.3	11.44 A.M.	135.0	96	98.1	135.0	180	99.0
	12.00 P.M.	78	98.2	12.44 P.M.	....	...	...	.....	96	98.8
F 16	7.40 A.M.	50	97.6	11.35 A.M.	133.75	98	98.2	133.75	192	98.6
	6.30 P.M.	69	98.7	12.35 P.M.	....	...	...	.....	77	99.3
	10.00 P.M.	59	97.8	.....	....	...	...	.....	...	...
G 17	7.10 A.M.	58	97.7	.....	....	...	...	.....	...	...
	11.25 P.M.	56	97.1	.....	....	...	...	.....	...	...
H 18	8.15 A.M.	65	97.2	.....	....	...	...	.....	...	...
	11.10 P.M.	52	96.3	.....	....	...	...	.....	...	...
I 19	7.45 A.M.	62	97.2	.....	....	...	...	.....	...	...
	2.00 P.M.	73	98.2	.....	....	...	...	.....	...	...
	10.50 P.M.	62	97.6	.....	....	...	...	.....	...	...

Table I is self-explanatory. The influence of the excessive exercise upon the temperature is clearly shown.

TABLE II.—WEIGHT AND NITROGEN CONTENT OF FOODS.

	May 11, A.			May 12, B.			May 13, C.		
Food materials.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.
Milk	1840.3	0.432	7.9500	1864.4	0.432	8.0542	1633.9	0.565	9.2315
Eggs	344.4	2.112	7.2737	267.4	2.112	5.6474	270.9	2.112	5.7214
Bread	96.5	1.2936	1.2484	50.0	1.2936	0.6468	59.7	1.3754	0.8211
Bread	...	....	....	60.1	1.3754	0.8466	42.5	1.6917	0.7179
Butter	17.5	0.350	0.0612	15.5	0.350	0.0542	20.0	0.350	0.0700
Malta-vita	51.0	2.918	1.4881	16.0	2.918	0.4668	16.3	2.918	0.4756
Banana	...	...	....	...	...	.....	202.0	0.208	0.4200
Sugar	13.8	....	....	15.0	....	.....	6.5	....	.....
Total N per day			18.0214			15.7160			17.4575

Food materials.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight per day. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.
	May 14, D.			May 15, E.			May 16, F.		
Milk	1281.1	0.535	6.8552	1207.6	0.547	6.6055	1265.3	0.565	7.0924
Eggs	231.8	2.112	4.8956	280.9	2.112	5.9326	309.6	2.112	6.5387
Bread	148.0	1.6917	2.5037	165.0	1.688	2.7852	151.0	1.52	2.2952
Butter	23.5	0.350	0.0822	54.3	0.350	0.1900	33.1	0.350	0.1158
Malta-vita	10.3	2.918	0.3005	...	....	.....	...	....	.....
Lemons	48.0	0.160	0.0768	69.0	0.160	0.1104	68.0	0.160	0.1088
Sugar	24.5	....	.....	36.6	....	.....	30.0	....	.....
Total N per day			14.7140			15.6237			16.1509
	May 17, G.			May 18, H.			May 19, I.		
Milk	1555.9	0.589	9.1642	789.6	0.576	4.5480	958.6	0.57	5.4640
Eggs	317.9	2.112	6.7140	310.9	2.112	6.5662	304.9	2.112	6.4394
Bread	54.0	1.52	0.8208	72.0	1.538	1.1073	52.0	1.213	0.6307
Bread	167.0	1.538	2.5684	179.0	1.213	2.1712	179.0	1.133	2.0280
Butter	41.6	0.350	0.1456	102.9	0.350	0.3601	71.9	0.350	0.2516
Malta-vita	...	....	.....	19.3	2.918	0.5631	...	....	.....
Lemons	40.0	0.16	0.0640	46.0	0.16	0.0736	49.0	0.16	0.0784
Bananas	...	....	.....	...	...	.....	202.0	0.208	0.4201
Sugar	32.0	....	.....	55.0	...	.....	57.0	....	.....
Total N per day			19.4770			15.3895			15.3122

TABLE III.—WEIGHT AND NITROGEN CONTENT OF URINE EXCRETED.

Date, May, 1902.	Weight of urine. Grams.	Specific gravity.		Per cent. of nitrogen. 1.	2.	Average.	Weight of nitrogen. Grams.
11 A	1784.3	$\frac{24.0° \text{ C.}}{24.2° \text{ C.}}$	1.0255	0.8623	0.8860	0.8741	15.5965
12 B	1147.3	$\frac{24.8° \text{ C.}}{24.8° \text{ C.}}$	1.0316	1.3577	1.3330	1.3453	15.4346
13 C	1253.3	$\frac{24.8° \text{ C.}}{24.8° \text{ C.}}$	1.0317	1.2868	1.2791	1.2829	16.0785
14 D	1193.4	$\frac{21.0° \text{ C.}}{21.0° \text{ C.}}$	1.0309	1.3980	1.3857	1.3918	16.6097
15 E	1001.3	$\frac{28.8° \text{ C.}}{28.8° \text{ C.}}$	1.0378	1.7301	1.6830	1.7065	17.0871
16 F	676.0	$\frac{28.2° \text{ C.}}{28.2° \text{ C.}}$	1.0466	2.2260	2.2290	2.2275	15.0579
17 G	1442.3	$\frac{27.4° \text{ C.}}{27.4° \text{ C.}}$	1.0285	1.1714	1.1785	1.1749	16.9455
18 H	1509.3	$\frac{24.8° \text{ C.}}{24.8° \text{ C.}}$	1.0223	0.9854	0.9670	0.9762	14.5979
19 I	1294.0	$\frac{28.0° \text{ C.}}{28.0° \text{ C.}}$	1.0304	1.0931	1.0650	1.0790	13.9622

A, B, C, first period of rest 47.1096
D, E, F, period of overexertion 48.7547
G, H, I, second period of rest 45.5056

NOTE.—Each date represents the urine collected in twenty-four hours, beginning with an empty bladder at 8.00 A.M., on the dates mentioned and including all that was passed from that time to and including that in the bladder at 8.00 A.M. the succeeding day. The analytical work began almost immediately after the last portion of each day's output was voided.

TABLE IV.—WEIGHT AND NITROGEN CONTENT OF DRIED FECES.

A, B, C period.			D, E, F period.			G, H, I period.		
Weight of dried feces. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight of dried feces. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.	Weight of dried feces. Grams.	Per cent. of nitrogen.	Weight of nitrogen. Grams.
41.0	3.169	1.2992	6.0	2.976	0.1785	14.0	3.65	0.5110
26.0	3.434	0.8928	12.0	3.379	0.4054	11.0	3.625	0.3987
13.0	3.0526	0.3968	18.0	3.42	0.6156	32.0	3.173	1.0153
11.0	3.571	0.3928	...	...	.....	...	....	.....
Total 91.0		2.9816	36.0		1.1995	57.0		1.9250
30.3 average		0.9938	12.0 average		0.3998	19.0 average		0.6416

NOTE.—The total nitrogen of each period, divided by three, furnishes the value used in obtaining the daily nitrogen balance (see Table V).

TABLE V.—INCOME AND OUTGO OF NITROGEN.

	Nitrogen.				
Date, May, 1902.	In food. Grams.	In feces. Gram.	In food assimilated. Grams.	In urine. Grams.	Gain + or loss —. Grams.
11 A	18.0214	0.9938	17.0276	15.5965	+1.4311
12 B	15.7160	0.9938	14.7222	15.4346	—0.7124
13 C	17.4575	0.9938	16.4637	16.0785	+0.3852
14 D	14.7140	0.3998	14.3142	16.6097	—2.2955
15 E	15.6237	0.3998	15.2239	17.0871	—1.8632
16 F	16.1509	0.3998	15.7511	15.0579	+0.6932
17 G	19.4770	0.6416	18.8354	16.9455	+1.8899
18 H	15.3895	0.6416	14.7479	14.5979	+0.1500
19 I	15.3122	0.6416	14.6706	13.9622	+0.7084
A, B, C, first period of rest			48.2135	47.1096	+1.1039
D, E, F, period of overexertion.			45.2892	48.7547	—3.4655
G, H, I, second period of rest...			48.2539	45.5056	+2.7483
Total gain during the experiment (nine days).....					+0.3867

TABLE VI.--NITROGEN AS AMMONIA, AS URIC ACID, IN XANTHINE SILVER PRECIPITATE, IN PHOSPHOTUNGSTIC ACID PRECIPITATE, IN FILTRATE FROM THE PHOSPHOTUNGSTIC ACID PRECIPITATE TREATED WITH SODIUM HYPOBROMITE, AS UREA (*a*) NaOBr METHOD, (*b*) BRAUNSTEIN'S METHOD.

Date, May, 1902.	Ammonia nitrogen. Grams.	Uric acid nitrogen. Gram.	Xanthine silver nitrogen. Gram.	Phosphotungstic precipitate nitrogen. Gram.	Phosphotungstic filtrate, NaOBr, nitrogen. Grams.	Urea (*a*) NaOBr, nitrogen. Grams.	Urea (*b*) Braunstein, nitrogen. Grams.
11 A	*	0.3834	0.4285	0.0662	*	12.7875	**
12 B	1.4721	0.2426	0.2062	0.2158	12.7207	11.7550	12.1712
13 C	0.5108	0.2434	0.2284	0.3002	13.0275	12.2613	13.8104
14 D	0.7219	0.3385	0.4013	0.1937	13.3597	12.7995	12.9025
15 E	0.7194	0.3053	0.3252	0.5008	13.6647	10.8473	13.7192
16 F	0.4309	0.3252	0.2311	0.1548	9.0667	11.5938	11.6234
17 G	1.0817	0.3190	0.3932	0.2818	11.8519	12.9817	**
18 H	1.0186	0.2931	0.1608	0.1941	11.1050	12.4524	**
19 I	0.5988	0.2361	0.2748	0.2791	9.2599	10.9623	10.0913
A, B, C	.....	0.8694	0.8631	0.5822	(first period of rest)		
D, E, F	1.8722	0.9690	0.9576	0.8493	(period of overexertion)		
G, H, I	2.6991	0.8482	0.8288	0.7550	(second period of rest)		

NOTE.—*Lost; **results entirely too large to be trustworthy—discovered too late to make another trial by this method.

Until analytical methods exhibiting greater accuracy than now at our command are developed all attempts to produce a balance sheet of the nitrogenous constituents of the urine will prove unsatisfactory.

TABLE VII.—THE P_2O_5, SO_3, AND Cl CONTENT OF THE URINE.

Date, May, 1902.	Volume, cc. at 25° C.	P_2O_5. Per cent.	P_2O_5. Grams.	SO_3. Per cent.	SO_3. Grams.	Cl_2. Per cent.	Cl_2. Grams.
11 A	1744.0	0.179	3.1247	0.166	2.9107	0.313	5.4714
12 B	1115.3	0.263	2.9340	0.237	2.6521	0.237	2.6489
13 C	1218.3	0.271	3.3030	0.233	2.8410	0.260	3.1742
14 D	1161.0	0.266	3.0929	0.250	2.9083	0.157	1.8314
15 E	967.5	0.324	3.1366	0.308	2.9857	0.228	2.2121
16 F	647.7	0.404	2.6218	0.410	2.6555	0.221	1.4359
17 G	1406.3	0.218	3.0657	0.197	2.7802	0.276	3.8885
18 H	1481.5	0.188	2.7948	0.174	2.5837	0.262	3.8864
19 I	1259.4	0.232	2.9250	0.197	2.4898	0.402	5.0671
A, B, C	.....	....	9.3617	....	8.4038	....	11.2945
D, E, F	.....	....	8.8513	....	8.5495	....	5.4785
G, H, I	.....	....	8.7855	....	7.8537	....	12.8420

TABLE VIII.—PERCENTAGE OF THE TOTAL NITROGEN PRESENT AS UREA, AMMONIA, URIC ACID, XANTHINE, AND PHOSPHOTUNGSTIC ACID PRECIPITATE. (Total nitrogen, 100 N_2 : the values given.)

	11 A.			12 B.			13 C.		
Urea (NaOBr)	81.98	....	....	76.16	....	....	76.25	....	....
Urea (NaOBr) P.F.*	....	**	....	....	82.41	....	....	80.43	....
Urea (Braunstein)	....	....	**	....	....	78.85	....	....	85.89
Ammonia	....	....	....	9.53	9.53	9.53	3.17	3.17	3.17
Uric acid	2.45	2.45	2.45	1.57	1.57	1.57	1.51	1.51	1.51
Xanthine	2.74	2.74	2.74	1.33	1.33	1.33	1.42	1.42	1.42
Phosphotungstic precipitate	0.42	0.42	0.42	1.33	1.33	1.33	1.86	1.86	1.86
Total accounted for	87.59	....	....	89.92	96.17	92.61	84.21	88.98	93.85
Unaccounted for	12.41	....	....	10.08	3.83	7.39	15.79	11.02	6.15
Total	100.00	....	....	100.00	100.00	100.00	100.00	100.00	100.00

	14 D.			15 E.			16 F.		
Urea (NaOBr)	77.06	....	....	63.48	....	....	76.99	....	....
Urea (NaOBr) P.F.*	....	80.43	....	....	79.97	....	....	60.21	....
Urea (Braunstein)	....	....	77.68	....	....	80.28	....	....	77.25
Ammonia	4.34	4.34	4.34	4.15	4.15	4.15	2.86	2.86	2.86
Uric acid	2.03	2.03	2.03	1.78	1.78	1.78	2.15	2.15	2.15
Xanthine	2.41	2.41	2.41	1.90	1.90	1.90	1.53	1.53	1.53
Phosphotungstic precipitate	1.16	1.16	1.16	2.93	2.93	2.93	1.02	1.02	1.02
Total accounted for	87.00	90.37	87.62	74.24	90.73	91.04	84.55	67.77	84.81
Unaccounted for	13.00	9.63	12.38	25.76	9.27	8.96	15.45	32.23	15.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	17 G.			18 H.			19 I.		
Urea (NaOBr)	76.60	....	....	85.80	....	....	78.51	....	....
Urea (NaOBr) P.F.*	....	69.94	....	....	76.07	....	....	66.32	....
Urea (Braunstein)	....	....	**	....	....	**	....	....	71.55
Ammonia	6.38	6.38	6.38	6.97	6.97	6.97	4.28	4.28	4.28
Uric acid	1.88	1.88	1.88	2.00	2.00	2.00	1.69	1.69	1.69
Xanthine	2.32	2.32	2.32	1.10	1.10	1.10	1.96	1.96	1.96
Phosphotungstic precipitate	1.66	1.66	1.66	1.32	1.32	1.32	1.99	1.99	1.99
Total accounted for	88.84	82.18	....	96.69	87.46	....	88.43	76.24	81.47
Unaccounted for	11.16	17.82	....	3.31	12.54	....	11.57	23.76	18.53
Total	100.00	100.00	....	100.00	100.00	....	100.00	100.00	100.00

NOTE.—P.F.* means filtrate from phosphotungstic acid precipitate treated with sodium hypobromite. ** Lost.

TABLE IX.—RATIOS.

Date, May, 1902.	100 N_2: P_2O_5.	100 N_2: SO_3.	100 N_2: Cl.	100 SO_3: P_2O_5.
11 A	20.0346	18.6625	35.0809	107.3521
12 B	19.0092	17.1828	10.6831	110.6293
13 C	20.5429	17.6695	19.7418	116.2618
14 D	18.6210	17.5096	11.2060	106.3473
15 E	18.3565	17.4734	12.3607	105.0540
16 F	17.4114	17.6352	9.5298	98.7309
17 G	18.0915	16.4067	22.9470	110.2690
18 H	19.1452	17.6991	26.6230	108.1704
19 I	20.9494	17.8324	36.2915	117.4793
A, B, C	19.8721	17.8388	23.9751	111.3984
D, E, F	18.1547	17.5357	11.2368	103.5300
G, H, I	19.3064	17.2587	28.2207	111.8644

TABLE X.—THEOBROMINE AND PURINE BASES OBTAINED BY KRÜGER'S METHOD.

	Grams theobromine nitrogen.	Grams copper precipitate, nitrogen.
13 C	0.0325	0.0151
14 D	0.0387	0.0027
15 E	0.1245	0.0001
16 F	0.5742	0.0086
17 G	0.2932	0.0041
18 H	0.0109	0.0064
19 I	0.0782	0.0106

In order to have a permanent record of a crystalline compound present in the urine during the period of overexertion, but not found in the urine of the other periods, except in the urine of the first day succeeding the middle period, microphotographs of the crystals were made, but their publication is withheld until the compound can be definitely identified. In appearance, these crystals closely resemble crystals of caffeïne and caffeïne nitrate; but the yield was too small to afford a quantity of pure crystals sufficient for a combustion. A nitrogen determination (by the absolute method) was made of a mixture of the crystals obtained from urines D, E, and F, by the Krüger[1] method; but, on account of impurities present, the result is not conclusive beyond the demonstration of the presence of nitrogen in the compound.

In an attempt to observe the melting-point, the mass darkened but did not liquefy at 250° C., but small needle-shaped crystals

[1] Martin Krüger: *Loc. cit.*

Total ..... 100.00 100.00 ....
NOTE.—P. F.* means filtrate from phosphotungstic acid precipitate treated with sodium hypobromite. ** Lost.

were found in the upper part of the tube when examined under the microscope.

Upon incineration, the D, E, F mixture yielded 63.43 per cent. ash (mostly sodium carbonate) and 36.57 per cent. (by difference) volatile organic substance.

0.0453 gram of substance gave 2.8 cc. nitrogen at 30° C., 751 mm., = 6.35 per cent. nitrogen. On this basis, the organic matter volatilized contained 17.36 per cent. nitrogen. This is entirely too low for caffeïne, but it closely approximates the amount of nitrogen found by Adolf Jolles[1] in the phosphotungstic acid precipitate of theophylline (17.04 per cent. nitrogen). Jolles contends that phosphotungstic acid precipitates only that portion of the purine bases in which the nitrogen is attached to the methyl groups, and that the remainder of the base is split off as urea. Thus far we have made no attempt to corroborate the work of Jolles, but shall give it attention in a subsequent investigation. On the basis of the original substance, the nitrogen found (6.35 per cent.) closely approximates the amount present in cynurenic acid—$C_{10}H_7NO_3 + H_2O = 6.76$ per cent. nitrogen; but the large amount of ash precludes this substance, as does also the method by which the crystals were obtained.

The crystals obtained by the method of Harper[2] from measured quantities of the corresponding twenty-four hours urine were well defined (some of them could be plainly seen with the unaided eye) but a brownish "smear" soluble in chloroform contaminated them, and the quantity obtained was too small to provide an amount of pure crystals sufficient for a combustion.

The second method is so much simpler than that of Krüger that an attempt will be made shortly to secure large quantities of this crystalline compound with a view to definitely determine its constitution.

SUMMARY.

1. The influence of fatigue-stuffs upon the pulse and temperature is shown in Table I. Similar observations have been repeatedly made. The subject complained of headache during the afternoon of D and the greater part of E and F.

[1] Adolf Jolles: *Ber. d. chem. Ges.*, **33**, 2119-2121.

[2] H. W. Harper: In the context of this communication—Analytical methods.

2. Tables II, III, and IV are self-explanatory. The urine of the entire experiment exhibited an acid reaction, was normal in color and odor. As would be expected, the specific gravity curved upward during the middle period, and this period was also marked by a copious deposit of urates. The diazo reaction was practically uniform throughout the entire experiment. The reaction for indican was faint except in the F and G urines—these contained notable quantities; most marked in G.

3. The income and outgo of nitrogen as shown in Table V presents some very interesting features:

(*a*) In the food eaten the nitrogen content was largest in that of the first period, smallest in that of the middle period.

(*b*) The total nitrogen assimilated was largest in the third period, smallest in the middle period.

(*c*) The action of the digestive tract upon the nitrogenous food was greatest during the middle period, least during the first period. Of the total nitrogen in the food consumed during the successive periods 94 per cent. was appropriated during the first period, 97 per cent. during the second period, and 96 per cent. during the third.

(*d*) The output of nitrogen was largest during the middle period, smallest during the third period.

(*e*) In the nitrogen balance there was a decided loss during the middle period, a gain during the other two periods—the third period showing the largest gain. Taking the nine days' experiment as a whole the subject made a small absolute gain in nitrogen. No permanent injury resulted from the experiment.

4. The results given in Tables VI and VIII are very interesting, but their discussion had best be postponed until an absolute method for the determination of urea, when mixed with its congeners, is devised.

5. While the results given in Tables VII and IX have no direct bearing upon the production of alkyl derivatives of xanthine during excessive muscular exercise they throw some light upon the chemical aspect of metabolism, and, therefore, are of value. The output of phosphoric anhydride was greatest during the first period of rest, and least during the last period. The subject did

more mental work during the first period than during either of the subsequent periods. It should also be borne in mind that he suffered with headache during the middle period and the beginning of the third period. It is not claimed that the increase in the output of phosphoric anhydride during the first period is due to mental exertion. While such an idea naturally suggests itself, no precautions were taken to safeguard this point, and the data here presented are too meager to warrant a conclusion thereon.

The output of sulphuric anhydride was greatest during the middle period, and least during the last period. The reverse of this is shown in the case of the chlorine. The decrease in the chlorine output during the middle period is very marked, as is also its rise in the last period. As far as we know, this observation is entirely new. The amount of sodium chloride daily consumed was practically uniform throughout the three periods (nine days total). The osmotic movement from the blood to the cutaneous emunctories during the period of excessive exercise may, in part, explain the facts observed; but it should be remembered that the daily period of excessive muscular exertion was of short duration.

The table showing the relative amounts of P_2O_5, SO_3 and Cl is particularly interesting. The 100 N_2 : P_2O_5, Cl, and the 100 SO_3 : P_2O_5 ratios seem to indicate that the role played by complexes containing these particular bodies is decidedly influenced by excessive exercise.

6. Evidence of the presence of methyl derivatives of xanthine is presented in Table X. This evidence finds further support in the microphotographs of a crystalline substance obtained from the phosphotungstic acid precipitate by the method of Krüger, and of those obtained by the chloroform method. The quantity of crystals obtained in a state of purity was insufficient for a combustion. However, a nitrogen determination (by the absolute method) was made of some of the contaminated crystals that we might at least prove or disprove the presence of nitrogen in the compound. The results obtained are given. It will be seen that the nitrogen is too low for any of the known methyl derivatives of xanthine. In the context will be found a fuller discussion of this point.

7. Thus far this investigation has thrown some new light upon the chemistry of fatigue, but much additional work is yet to be done before the theoretical discussion of the results may be profitably entered upon. The inquiry will be further pursued in this laboratory.

In conclusion the authors acknowledge their sincere thanks for assistance rendered by Messrs. F. C. Beall, O. D. Hargis, H. Kuehne, and M. B. Wesson.

NOTE.—This communication is dated June, 1902, because the experimental part was complete by that time. However, the results were not put in their present shape for publication until September, 1902, the duties incident to the close of the session making it impossible to shape the results at an earlier date.

THE UNIVERSITY OF TEXAS, CHEMICAL LABORATORY,
AUSTIN, TEXAS, June, 1902.

ON THE FIXATION OF AMMONIA AND POTASH BY HAWAIIAN SOILS.

BY J. T. CRAWLEY AND R. A. DUNCAN.

Received September 30, 1902.

IN this Journal, **24**, 1114, will be found a paper by the writer on the "Fixation of Phosphoric Acid in the Soil." This paper will record results on the fixation of the other chief fertilizer constituents, ammonia and potash. The same methods described in that work were followed in these experiments, and the results, therefore, can be compared with each other. The main object is to find the depth in the soil at which the chief fertilizing materials are fixed and to determine the loss by drainage when the application is followed by a heavy irrigation. A given weight of the commercial article containing ammonia and potash, namely, sulphate of ammonia and sulphate of potash, is applied to the soil, and this is irrigated with 3 or 4 inches of water (the usual irrigation as practiced on the plantations), the drainage collected and analyzed. The difference between the amount applied and that found in the drainage is the amount abstracted or held by the soil. By varying the depth of soil we find the depth at which the ingredients are fixed. Boxes (9 inch cube) with holes in the bottom for the escape of water were used in the experiment. In all cases

4800 cc. of water were poured upon the soil, and the time necessary for the excess to drain off is given.

I. FIXATION OF AMMONIA.

Ten grams of commercial sulphate of ammonia, containing 2.478 grams ammonia were used in each case.

(1) Six inches of soil; the sulphate was scattered over the soil and 4800 cc. water were added; 1130 cc. drained through within seventeen minutes, containing 0.0038 gram ammonia or 0.155 per cent. of total applied.

(2) Four inches of soil; drainage was completed in twelve minutes; 2180 cc. water passed through, containing 0.0464 gram ammonia or 1.387 per cent. of total.

(3) Two inches of soil; drainage was completed in thirteen minutes; 3280 cc. water were recovered, containing 0.3400 gram ammonia, or 13.88 per cent of total.

(4) One inch of soil; drainage was completed in seventeen minutes; 4000 cc. water were recovered, containing 1.2328 grams ammonia, or 49.79 per cent. of total.

Putting these results together, we have:

TABLE I.—FIXATION OF AMMONIA.

Depth of soil. Inches.	Ammonia retained. Per cent.
6	99.85
4	98.13
2	86.12
1	50.21

In these experiments we see that with irrigation following the application of sulphate of ammonia, one-half is retained in the first inch, more than four-fifths within the first 2 inches and almost all within 4 inches of soil.

In order to determine if the ammonia retained has been firmly fixed and is insoluble in water, the 1 inch of soil which had already been irrigated once was subjected to further irrigations, with the following results:

TABLE II.—AMOUNT OF AMMONIA WASHED FROM THE FIRST INCH OF SOIL BY SUCCESSIVE IRRIGATIONS.

Number of irrigations.	Ammonia washed out. Grams.	Per cent.
First	1.2328	49.79
Second, three days after first	0.1937	7.8
Third, one hour after second	0.1249	5.0
Fourth, nineteen hours after third	0.0904	3.6
Fifth, one hour after fourth	0.0581	2.3
Total, five irrigations	1.6999	68.49

The ammonia is held rather firmly, but subsequent irrigations wash it out in decreasing quantities.

II. FIXATION OF POTASH.

Ten grams sulphate of potash containing 4.8 grams actual potash were scattered over the soil, and water was poured over, as in preceding tests.

TABLE III.—FIXATION OF POTASH.

Depth of soil. Inches.	Potash retained. Per cent.
6	98.55
4	94.18
2	82.03
1	69.19

Seven-tenths of the potash applied is retained in the first inch, more than four-fifths in 2 inches and almost all within 6 inches of the soil. The box containing 6 inches of soil which had been irrigated once, was subjected to further irrigations to see if the potash is held firmly.

TABLE IV.—AMOUNT OF POTASH WASHED FROM SIX INCHES OF SOIL BY SUCCESSIVE IRRIGATIONS.

Number of irrigation.	Potash washed out.		Potash in 1000 cc. drainage.
	Grams.	Per cent.	Grams.
First	0.0697	1.45	0.0680
Second, 4 days after first	0.1631	3.4	0.2044
Third, 1 hour after second	0.1659	3.5	0.0361
Fourth, 16 hours after third	0.1302	2.7	0.0296
Fifth, 1 hour after fourth	0.1139	2.4	0.0243
Sixth, 7 days after fifth	0.0929	1.9	0.0251
Seventh, 2 days after sixth	0.0948	2.0	0.0228
Eighth, 7 days after seventh	0.0967	2.0	0.0215
Total, 8 irrigations	0.9272	19.35	

As the moisture content of the soil varies, the amount of drainage will vary. Therefore I have included in the table the amount of potash in each 1000 cc. of drainage. As in the case of ammonia, the potash is held rather firmly but irrigations gradually wash it away, light irrigations having washed 19 per cent. out of 6 inches of soil.

Below will be found the results on phosphoric acid, ammonia, and potash.

TABLE V.—FIXATION OF PHOSPHORIC ACID, AMMONIA AND POTASH.

Depth of soils.	Phosphoric acid retained. Per cent.	Ammonia retained. Per cent.	Potash retained. Per cent.
6	99.43	99.84	98.55
4	....	98.13	94.18
3	91.25	....	....
2	....	86.12	82.03
1	53.35	50.21	69.19

These results have a great practical bearing on plantation work in these islands. Many of the plantations depend upon irrigation entirely, and a great deal of the water, as I have shown in an article in the August number of the *Hawaiian Planter's Monthly* on "The Water-Holding Power, and the Irrigation of Hawaiian Soils," passes directly and immediately through the soils. In other cases, as in the Hilo district, the soils are subjected to very heavy rains. Were the soluble fertilizer ingredients not fixed at once the loss would be very great; but the experiments show that even under heavy washings they are fixed very rapidly. But the solubility of these substances in water after the first irrigation, though slight, emphasizes the importance of keeping the irrigation well under control. The nitrogen of sulphate of ammonia is gradually changed to nitrate, and most of that which the plant has not assimilated is washed away by the first irrigation or heavy rainfall. The phosphoric acid is more firmly bound, and the loss of this substance is very slight. Under the conditions of the tests, 19 per cent. of the potash applied as sulphate was washed below 6 inches by eight irrigations.

We thus see that heavy and repeated irrigations wash out the available ammonia and potash; and this will partially account for the fact that very often the effects of a fertilizer, especially of a nitrogenous fertilizer, are not lasting.

HONOLULU, H. I.

A PROBABLE CAUSE OF THE DIFFERENT COLORS OF IODINE SOLUTIONS.

BY ARTHUR LACHMAN.

Received September 30, 1902.

IT is a well-known fact that solutions of free iodine have different colors, depending in some way upon the nature of the solvent.

Gautier and Charpy,[1] who investigated this problem about twelve years ago, distinguished four sets of colors, of the following types:

(1) Violet, *e. g.*, chloroform; (2) red, *e. g.*, ethylene bromide; (3) red-brown, *e. g.*, toluene; (4) brown, *e. g.*, alcohol.

A large number of solvents were thus classified, but the authors confessed themselves unable to find any relations between the chemical function of the solvent and the color. The following year, Rigollot[2] determined the absorbing power of different iodine solutions for definite light-waves; but his results led to no explanation. A few years later, an elaborate study of the problem was undertaken by Krüss and Thiele[3] They ascertained the molecular weight of iodine in various solvents, and found that practically in all cases, where moderately dilute solutions were taken, the iodine molecule consists of 2 atoms. Variations from this value were irregular, both for brown and for violet solutions. Concentrated solutions usually gave high molecular weights, indicating association, but no change of color accompanied this association.

In spite of these results, Krüss and Thiele attempt to explain the different colors by an assumption of different molecular weights: violet solutions containing I_2, brown solutions $(I_2)_n$, n being greater than 1. These complicated molecules, however, are supposed to give a normal molecular weight by all osmotic methods. This explanation is equivalent to saying that in brown solutions the molecular weight of iodine is much greater than in violet, but that none of our present methods are able to demonstrate the increase; and it involves a conception of the molecular theory whose utility yet remains to be shown. The change from brown into violet is ascribed to dissociation; if the above theory is correct, solvents with brown color should have less dissociating power than those with violet. But this is contradicted by well-established facts; alcohol has much greater dissociating power than chloroform or benzene.

Notwithstanding the negative results of Gautier and Charpy, and of Krüss and Thiele, a simple causal connection seems to exist between the chemical behavior of the solvent and the color

[1] *Compt. Rend.*, **110**, 189; **111**, 645 (1890).
[2] *Ibid.*, **112**, 38 (1891).
[3] *Zischr. anorg. Chem.*, **7**, 25 (1894).

of iodine solutions. This relationship was not apparent to the above investigators *because in critical cases they observed wrong colors,* owing to impurities in the solvents. From the table given below, it will be seen that iodine solutions, when made with pure solvents have but two colors—violet and brown—with but one exception, which will be discussed below.

COLOR OF IODINE IN VARIOUS SOLUTIONS.

A. Violet Solutions.

Hydrocarbons :
- Hexane
- Benzene (thiophene free)
- Toluene[1]
- *o*-Xylene[2]
- *m*-Xylene
- *p*-Xylene

Halogen compounds :
- Chloroform
- Ethylene chloride[3]
- Ethylidine chloride
- Tetrachlorethylene[4]
- Carbon tetrachloride
- Isobutyl chloride[5]
- Amyl chloride
- Chlorbenzene
- Benzalchloride
- Benzotrichloride

- Bromoform
- Ethylene bromide[5,6]
- Trimethylene bromide
- Amyl bromide[5]
- Brombenzene

Nitro compounds :
- Nitroethane
- Nitropropane
- Tetranitromethane
- Isobutyl nitrate

Sulphur compound :
- Carbon bisulphide

[1] Gautier-Charpy, red-brown.

[2] Thiele-Krüss, wine-red (xylenes not separated).

[3] Gautier-Charpy, Krüss-Thiele, red.

[4] Tetra-chlorethylene, C_2Cl_4, is the only substance in the above list which is unsaturated in structure. Its easy formation during chlorination reactions indicates that its unsaturated character is more formal than real, in spite of its double bond.

[5] Ethylene bromide, amyl bromide, and isobutyl chloride required careful purification before giving violet solutions. The impure solvents, which gave red solutions, all decolorized permanganate.

[6] Gautier-Charpy, Krüss-Thiele, red.

B. Brown Solutions.

Iodides :
- Ethyl iodide
- Amyl iodide
- Cetyl iodide
- Phenyl iodide
- Potassium iodide } In water
- Hydrogen iodide } solutions

Oxygen compounds.

Alcohols :
- Methyl alcohol
- Ethyl alcohol
- *n*-Butyl alcohol
- Dimethylethyl carbinol
- Heptyl alcohol

Ethers :
- Ethyl ether
- Dimethyl acetal
- Anisol
- Phenetol

Ketones :
- Acetone
- Methylethyl ketone
- Diethyl ketone
- Acetaldoxime
- Acetophenone

Acids and esters :
- Formic acid
- Acetic acid
- Lactic acid
- Caproic acid
- Ethyl acetate
- Amyl acetate
- Isobutyl isobutyrate

Sulphur compounds :
- Amyl mercaptan
- Thiophene

Nitrogen compounds.

Nitriles :
- Acetonitrile
- Propionitrile
- Capronitrile
- Benzonitrile

Nitrilo-bases :
- Pyridine
- Quinoline

From the results tabulated above, all of which have been verified personally, the relationship between color and the constitution of the solvent stands out clearly: *saturated solvents give violet, solvents which have unsaturated character give brown solutions.* In the first, or violet class, we find hydrocarbons, their chlorides and bromides, and carbon bisulphide; and also, strange to say, the *nitro compounds.* All the other oxygen compounds, so far as investigated, give brown solutions. The brown solvents comprise the alcohols, ethers, ketones, acids and esters; nitriles and nitrilo-bases; alkyl and other iodides; and bivalent sulphur compounds.

The iodine molecule, as found in iodine vapor, is violet; we have every reason for assuming that in its violet solutions iodine is in a state of normal physical distribution. On the other hand, certain of the brown solutions are known to contain periodides, usually of the form $(MX).I_2$; among these are potassium iodide, phenyl iodide, and the tertiary bases. Nitriles have long been known for their additive properties in general; and in the case of oxygen compounds, the recent startling results of Baeyer and Villiger[1] have fully demonstrated the hitherto unsuspected additive powers of combined oxygen atoms. It seems quite justifiable to assume in all brown iodine solutions the existence of (probably unstable) addition products whose general composition is

$$\text{Molecule-solvent} + I_2.$$

Such an explanation was indeed offered some years ago by Beckmann,[2] and considered and rejected by Krüss and Thiele. If it is assumed, as it was by Beckmann, that the *whole* of the iodine thus adds to the solvent, the effect upon the *observed* molecular weight would be a marked decrease (as a consideration of Raoult's formula shows), contrary to the measurements of Krüss and Thiele. But there is no need to make this assumption; a very small amount of alcohol suffices to change the color of an iodine-chloroform solution, and 3 per cent. of alcohol give as dark a brown as can be obtained with pure alcohol.

EFFECT OF ABSOLUTE ALCOHOL ON COLOR OF IODINE IN CHLOROFORM.

Alcohol. Per cent.	Color.
3.5	Brown
0.4	Red
0.2	Mixed red and violet
0.1	Violet

[1] *Ber. d. chem. Ges.*, **34**, 2679 (1901).

[2] *Ztschr. phys. Chem.*, **5**, 76 (1889).

The iodine in brown solutions is therefore probably in a condition of equilibrium between pure solution and the addition product

$$\text{Solvent} + I_2 \rightleftarrows (\text{Solvent} + I_2),$$

very much like many double salts, or like the chlorine ions[1] in green chromium chloride hexahydrate.

The view here presented, that brown solutions contain some addition product, and violet solutions simple iodine molecules, is borne out by an important fact: Brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently.[2] As heat produces dissociation, and cold induces association, the facts are in excellent agreement with expectation.

The actual isolation of the addition products of iodine with oxygen compounds will probably be difficult, but an effort in this direction will be made as soon as possible. Schützenberger[3] has described an addition product of bromine and ether, and iodine may behave similarly.

Two points remain for discussion. In the first place, the behavior of the nitro compounds seems to put them apart from other oxygen compounds. The structure of the nitro group is still uncertain, but numerous reactions show that its oxygen atoms are quite active, and possess considerable additive power.[4] Their indifference to iodine will be investigated more closely later on.

The second point is the behavior of ethyl bromide towards iodine. In spite of numerous efforts, I have not been able to prepare this substance in a state sufficiently pure to obtain with it a violet iodine solution; in every case, the solution is dark red. Ethyl bromide is made by two methods; the distillation of ethylsulphuric acid with potassium bromide also forms ether, which cannot be separated by the most careful fractioning; and the action of phosphorus bromide upon alcohol yields ethyl bromide contaminated with phosphorus, which resists hours of boiling with moist sodium amalgam. I am confident, however, that ethyl bromide will prove no exception to the above classification of

[1] Werner: *Ber. d. chem. Ges.*, **34**, 1579 (1901).

[2] Krüss and Thiele: *Loc. cit.*, p. 72; Gautier and Charpy: *Compt. Rend.*, **111**, 645 (1890); Wiedemann: *Wied. Ann. Phys.*, **269**, 580.

[3] *Compt. Rend.*, **78**, 1511 (1873); *Ann. Chem.* (Liebig). **167**, 86 (1873).

[4] Lachman: *Am. Chem. J.*, **21**, 443 (1899); This Journal, **23**, 897 (1901); Angeli: *Ber. d. chem. Ges.*, **29**, 1884 (1896); Meisenheimer: *Ann. Chem.* (Liebig), **323**, 205 (1902).

iodine solvents, for similar difficulties were met, during this investigation, with amyl bromide and ethylene bromide. The first samples of these substances gave dark red iodine solutions, but after careful purification, pure violet solutions were obtained.

SAN FRANCISCO, September 13, 1902.

[CONTRIBUTIONS FROM THE NEBRASKA EXPERIMENT STATION, NO. 1.—SENT BY E. A. BURNETT.]

PRUSSIC ACID IN SORGHUM.

BY HENRY B. SLADE.

Received October 3, 1902.

INSTANCES of the fatal effects of green sorghum upon stock are frequently reported. The Nebraska Experiment Station records 144 fatal cases in a single year. "At Imperial 10 cattle out of a herd of 32 died suddenly. At Culbertson 11 cattle died within an hour from eating cane. At Wauneta a stockman reports the loss of 7 head out of a small herd."[1] From Australia like cases are reported.[2] In one instance 17 animals in a single herd died from eating sorghum; in other instances cattle were allowed to feed upon the cane without loss. Berthelot and André in 1886, in an article on "The Noxious Effects of Sorghum,"[3] ascribed the cause to excessive amounts of potassium nitrate. The late Mr. Williams, of the U. S. Department of Agriculture, also suggested saltpeter as the cause of the trouble.[4] Determinations of the potassium nitrate in poisonous sorghum by Hiltner[5] showed that the amount present was inadequate to the effect produced and the idea was presented that "the plant under certain conditions develops a highly poisonous chemical compound." In a paper before the Nebraska Section of the American Chemical Society[6] the theory was put forward by the writer, in the fall of 1901, that such a poisonous compound might be produced by the action of an enzyme upon a glucoside formed in the plant through a process of abnormal growth.[7] An examination of a sample of sorghum

[1] Nebraska Experiment Station Bulletin No. 63.

[2] Quoted in Experiment Station Record, **13**, 992.

[3] Abstract in Biedermann's *Centralblatt*, **22**, 470.

[4] Farmers' Bulletin No. 50, p. 17.

[5] Nebraska Experiment Station Bulletin No. 63.

[6] Nebraska Experiment Station, 15th Annual Report, p. 55.

[7] Dunstan and Henry have since confirmed this view in the case of the Great Millet or Sorghum Vulgare of Egypt. Since the above article was contributed the attention of the

from a lot which had proved fatal to cattle showed the presence of prussic acid. A further study appears to verify the view that the acid is split off from a compound through ferment action and a preliminary report of the results is now given.

The sample in question was received at the Station the fourth day after it had been cut. A portion was crushed by means of a sausage grinder, macerated with water for an hour and the filtered extract distilled into sodium hydroxide. On the addition of ferrous and ferric salts and acidulating with hydrochloric acid the characteristic blue color of the ferrocyanide of iron was obtained. The test was repeated with separate stalks with like results in every case. The prussic acid was also obtained as the nitroprusside and as silver cyanide. No prussic acid could be obtained from the water extracts of the roots but leaves and stalks both gave good tests, more marked in the stalks which appeared to yield the greater amount of the acid.

The same sample after drying in the laboratory for twelve days still yielded a decided test for prussic acid. Another sample of sorghum cut at the same time and cured in the field for six days and in the laboratory for twelve days likewise produced the acid on following the same procedure as in the other cases. The fact that the sorghum, if dried without crushing, still retains the power to produce prussic acid indicates the localization of the enzyme and acid-producing compound in separate cells of the plant. Quantitative estimations of the yield of prussic acid were made by macerating single stalks in a crushed condition for twelve hours in rubber-stoppered flasks. The acid formed was distilled into dilute sodium hydroxide and the amount of cyanide determined by titration with silver nitrate according to Liebig's method as directed by Fresenius.[1] By this procedure 0.013 per cent. of prussic acid was obtained in one case and 0.014 per cent. in

writer has been called to the work of the two English investigators who have isolated a glucoside, dhurrin, which breaks up under the action of an enzyme with the formation of prussic acid. (*Chemical News*, June 27, 1902.) From the brief account of the properties given, dhurrin does not seem to be identical with the prussic acid-forming glucoside of American cane. Dr. Samuel Avery, of the Nebraska Agricultural Experiment Station, in a private communication to the writer, states that under certain conditions the glucoside from American sorghum is decomposed by boiling hot water, which is not the case with dhurrin. It would be interesting to know whether the various glucosides yielding prussic acid form a chemical series similar to those of the saponin bodies worked out by Kobert.

[1] "Quantitative Analysis," p. 450.

another. On this basis a kilogram of sorghum would contain over twice the maximum medicinal dose for cattle, of the anhydrous acid and might prove fatal. Frohner[1] places the fatal dose at 0.5 to 1 gram. At this rate 3.5 kilos of the cane would be extremely dangerous. A cow turned into the patch from which the above samples were taken developed the most marked symptoms of prussic acid poisoning after eating only a small amount of the cane. In the light of these results there would seem to be but little question that the poisoning of stock by sorghum is due to the prussic acid yielded by the plant.

The question still remains as to the formation of the prussic acid in the sorghum. Robiquet and Boutron-Charlard[2] found prussic acid in oil of bitter almonds, and in 1837 Liebig and Wöhler[3] discovered that the prussic acid was formed by the action of the emulsin upon the amygdalin in the almonds. Since that time prussic acid has been found in various plants and its formation has been generally ascribed to the action of emulsin upon some glucoside. In 1900 Dunstan and Henry[4] discovered a new prussic acid-producing enzyme in the Egyptian vetch (*Lotus arabicus*) which they call lotase. Lotase splits up the glucoside, lotusin, with the production of prussic acid, a yellow coloring-matter, lotoflavin, and dextrose. Cattle in Northern Africa are oftentimes fatally poisoned by eating the vetch up to the time of the ripening of the seed. After that time the glucoside disappears and the plant becomes harmless.[5]

In the case of sorghum the poison seems to be formed by the action of an enzyme upon a glucoside. The fact that the dried plant still yielded prussic acid shows that it does not exist in that form in the plant. To determine whether the acid was formed by chemical or ferment action, extracts were made by digesting 20 grams of the sorghum pulp with 250 cc. of water at the temperature of the laboratory and also by pouring boiling hot water upon a like amount of pulp and boiling for five minutes. Both were allowed to macerate and then distilled as usual into

[1] "Lehrbuch der Toxicologie," p. 860.
[2] Quoted by Oppenheimer: "Ferments and Their Actions," English translation, p. 209.
[3] *Ann. Chem. Pharm.*, **21**, 96; **22**, 17.
[4] Royal Society Proceedings, **67**, 224; **68**, 374.
[5] Thanks are due to Mr. V. K. Chesnut, of the Poisonous Plants Division of the U. S. Department of Agriculture, for this reference.

sodium hydroxide. The former gave the usual marked test for the acid but the extract which had been boiled gave only the slightest trace of acid, the acidulated solution yielding only a faint green color after standing for some time. The formation of the prussic acid hence appeared due to a ferment action. However, as the compound producing the acid might be decomposed by simply boiling and the prussic acid formed thereby escape, extracts were also prepared with 95 per cent. alcohol, 2 per cent. sodium hydroxide, 0.4 per cent. hydrochloric acid, 0.2 per cent. sodium carbonate and 0.5 per cent. sodium chloride. In each of these tests 20 grams of the sorghum pulp and 250 cc. of the solvent were taken and a few drops of chloroform added to prevent bacterial action. The sorghum was introduced into the solvent so soon as it had been reduced to a pulp with a sausage grinder and the digestion continued for three days in glass-stoppered bottles at the room temperature; the liquid rapidly filtered through linen into a flask and distilled into sodium hydroxide. In the case of the alkaline extracts the liquid was rendered acid with dilute sulphuric acid before distilling. Neither the acid nor alkaline extracts showed a trace of prussic acid as was also the case with the alcoholic extract. On the other hand the sodium chloride extract gave a distinct test. If the formation of the acid were due to simple chemical decomposition through boiling, tests for the acid should have been obtained in every case. On the other hand the slight trace only of acid found in the boiled extract and the known hindering action of acids and alkalies as well as the favorable action of sodium chloride upon ferment action point to this as the source of the prussic acid. The behavior of the ferment in these respects would serve to identify it as emulsin but an extract with 40 per cent. alcohol yielded prussic acid while emulsin is sensitive to the presence of 8 per cent. alcohol.[1] In studying the enzymes of sorghum the active preparations from the plant had no action upon amygdalin, from which the absence of emulsin was inferred.[2] The active agent in this case may be a special form of emulsin such as that described by Jorrisen and Hairs[3] or possibly a new enzyme. It does not appear to be ordinary emulsin. The glucase of sorghum acts upon

[1] Effront: "Enzymes and Their Applications," English translation, 1, 270.
[2] Nebraska Experiment Station, 15th Annual Report, p. 61.
[3] Quoted by Oppenheimer, p. 210.

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From the above sample of poisonous sorghum, an enzyme preparation was obtained by precipitating the sorghum juice with 95 per cent. alcohol and again precipitating the alcoholic filtrate. The impure preparation thus obtained gave a decided blue color, which rapidly developed, with freshly-prepared tincture of guaiac and hydrogen peroxide but not after boiling the solution of the ferment. With various preparations from the sorghum this formed no prussic acid. The same preparations likewise gave negative tests for the acid after boiling with dilute mineral acids, neutralizing and testing with Fehling's solution. In every case where prussic acid was formed, the extract gave a rose-red color with strong hydrochloric acid in excess or with concentrated sulphuric acid. In the extracts where no prussic acid was formed no such reaction could be obtained. The most intense color was obtained from the water extracts of the stalks which was prepared by cutting off the stalks for four inches above the roots into small, quarter-inch pieces and macerating with water for an hour. This substance appears to be a coloring-matter formed together with the prussic acid by enzyme action. With alkalies the color produced by the acid disappears and returns on acidulating. With nitric acid the red color disappeared and on reducing the red hydrochloric acid solution of the substance with zinc dust no color appears on neutralizing.

This coloring-matter is precipitated by lead subacetate from which it may be again obtained by treating the precipitate suspended in water with hydrogen sulphide and treating the lead sulphide with hydrochloric acid. By filtering, neutralizing and extracting the residue with alcohol the compound may be isolated. The lead precipitate gives the characteristic brilliant rose-red with hydrochloric and sulphuric acids.

Thus far the suspected glucoside of American cane has not been isolated and the evidence for its existence rests upon the formation of prussic acid and a coloring-matter under the conditions described together with the general experience of the formation of prussic acid in plants. The evidence thus far at hand points to ferment action as the cause.

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DERIVATIVES OF PHENYLETHER. V.

By Alfred N. Cook.

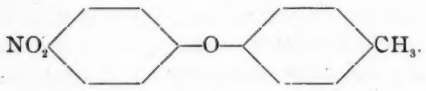
Received October 6, 1902.

For some time past I have been engaged in the study of the derivatives of phenylether, using a reaction that is of common application in both the fatty and aromatic series, that of treating a fatty or aromatic haloid with an alcoholate or phenolate of an alkali metal. An ether is formed and an alkali salt of a haloid acid is precipitated according to the following equation:

$$RBr + KOR' = ROR' + KBr.$$

It has been found[1] that an aromatic bromide or chloride containing a nitro group in the ortho or para position reacts with great readiness upon potassium phenolates to produce derivatives of phenylether. During the past three years I have extended this method to the cresols. Success has attended each attempt to combine a potassium cresolate with a bromnitrobenzene, and each of the mother substances has yielded a number of derivatives.

4-NITRO-4′-METHYL PHENYLETHER,



This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared as described in a previous article.[2]) Equimolecular quantities of the two reacting substances were heated together in an oil-bath. Action began at 110°, as was shown by the agitation of the fused mass, and rose during the action to 125°. The phenylether could not be extracted from the precipitated potassium bromide with ethyl ether as had been previously done with its analogues, on account of its sparing solubility in that menstruum, and it was found that the substance could be separated from the parabromnitrobenzene not acted upon, and other substances, by simple fractional distillation under diminished pressure, instead of distilling them off with steam as had been previously done in analogous cases. The

[1] *Ber. d. chem. Ges.*, **29**, 1446 and 1878.

[2] *Am. Chem. J.*, **24**, 526.

method was afterwards found to give good results with other analogues, as has already been described in the two previous papers. The yield was about 1.25 grams of the nitromethylphenylether for every gram of the cresol used. After purifying as much as possible by repeated fractional distillation *in vacuo*, it was crystallized several times from hot alcohol.

4-Nitro-4′-methyl phenylether is a sulphur-yellow, crystalline substance which speedily turns brown on exposure to light, and melts at 66°. It is soluble in benzene, sparingly soluble in sulphuric ether, and insoluble in petroleum ether. It is much less soluble in cold than in hot alcohol which renders it very readily crystallized. It boils at 225° under a pressure of 25 mm. It has no taste but feels like sulphur when taken into the mouth. It had an odor of parabromnitrobenzene from which it could not be freed by fractional distillation and repeated crystallization from alcohol. An attempt to oxidize the side-chain to carboxyl by means of chromic acid in acetic acid solution was unsuccessful. The substance was entirely destroyed. An analysis gave 6.27 per cent. N; calculated, 6.11 per cent.

4-NITRO-4′-METHYL PHENYLETHER SULPHONIC ACID,

$$CH_3.NO_2.C_{12}H_7O.SO_3H,$$

was prepared by the same method as its analogues described in previous papers. When a solution of the acid was evaporated to a small bulk it separated as a thick, red, syrupy liquid which, when dissolved in hot water, crystallized in light yellow needles which melted at 102°. A water solution is much yellower than the substance itself. 8.4 parts of the acid are soluble in 1000 parts of water at 80°. The purified acid is almost tasteless in the solid form, while the syrupy liquid has a sharp odor and taste, probably due to decomposition products formed during evaporation. Its composition was determined by the analysis of the barium salt.

The barium salt, $(CH_3.NO_2.C_{12}H_7O.SO_3)_2Ba + 2H_2O$, was prepared by the method described in previous papers. It crystallizes from a water solution in warts of a light yellow color which turn brown on exposure to light, if but slightly moist. The substance has a bitter taste and its water solution is yellow. 20.8 parts of the salt are soluble in 1000 parts of water at 15°, and

128.6 parts are soluble in 1000 parts of water at the temperature of the boiling water-bath. When heated in the air-bath at 100° it turns to a sulphur-yellow color and loses in weight corresponding to 1 molecule of water of crystallization. At this stage it is hygroscopic and when exposed to the air increases to its original weight. When heated to 168° it loses in weight corresponding to a second molecule of water and becomes white. At this stage it is not hygroscopic. The loss in weight is permanent. Two analyses of the salt desiccated over sulphuric acid resulted as follows:

	Calculated for $(C_{13}H_{10}O_6NS)_2Ba + 2H_2O$.	Found. I.	II.
Barium	17.36	17.29	17.21
Water at 100°	2.28	2.46	2.49
Water at 168°	2.28	2.23	2.33

The sodium salt, $CH_3.NO_2.C_{12}H_7O.SO_3Na + 3\frac{1}{2}H_2O$, was prepared by precipitating the barium from a water solution of the barium salt with sodium carbonate. The water solution is more intensely yellow than that of the barium salt. On evaporating to a small bulk it crystallized out in radial aggregations of leaf-like crystals. It is soluble in alcohol and 62 parts of the salt are soluble in 1000 parts of water at 20° C. After desiccation over sulphuric acid it was heated in the air-bath to 100°, when it lost in weight corresponding to 3.5 molecules of water of crystallization. Two determinations of the water of crystallization resulted as follows:

	Calculated for $C_{13}H_{10}O_6NSNa + 3\frac{1}{2}H_2O$.	Found. I.	II.
Water	15.99	15.97	15.97

4-AMINO-4′-METHYL PHENYLETHER, $NH_2.C_6H_4OC_6H_4.CH_3$, was prepared from the hydrochloride salt mentioned below by precipitating from a water solution with ammonium hydroxide. It is a snow-white substance which is soluble in alcohol, insoluble in ether, and melts at 122°. It is soluble in hot water from which it crystallizes on cooling in white flakes.

The hydrochloride salt was prepared from the corresponding ether by reducing with tin and hydrochloric acid in alcoholic solution while warming on the water-bath, and precipitating the tin with hydrogen sulphide. It showed some tendency to decompose while evaporating to crystallization. It is very soluble in water

but does not crystallize from it successfully. It crystallizes readily from a hot solution of strong hydrochloric acid in long needles or glistening flakes.

The hydrobromide was formed by dissolving the free amino compound in hydrobromic acid. Its appearance is very much like the hydrochloride. The amino compound dissolves with some difficulty in dilute sulphuric acid to form the *sulphate.* It crystallizes out in glistening flakes. The *nitrate,* formed in a similar manner, crystallizes from the acid solution, on cooling, in flat needles.

The platinum salt, $(CH_3.C_6H_4OC_6H_4.NH_2)_2.H_2PtCl_6 + H_2O$, was prepared by adding a solution of chlorplatinic acid to a strong solution of the hydrochloride. It does not precipitate immediately, unless the solutions are very strong, but in a few minutes fine yellow crystalline needles are formed. When moist it turns brown in diffused light, but when dry the direct sunlight does not affect it. The melting-point is 195°. When heated to 100° in an air-bath it became dark colored and lost in weight corresponding to 1 molecule of water of crystallization. Analyses for platinum and water resulted as follows:

	Calculated for $(C_{13}H_{13}NO)_2.H_2PtCl_6 + H_2O$.	Found. I.	II.
Platinum.....	23.61	23.40	23.85
Water at 100°.....	2.18	2.47	....

NITRO-4-NITRO-4′-METHYL PHENYLETHER, $(NO_2)_2.CH_3.C_{12}H_7O$.

Strong nitric acid was added to a quantity of 4-nitro-4′-methyl phenylether when the temperature rose 2°-3° and the acid turned to a reddish color, the ether apparently dissolving slightly in the acid. On heating to 80°-90° a violent action began, dense brown fumes being given off, which subsided after a few minutes, and there resulted a deep orange-red liquid. On adding water a yellow oil was precipitated, which, on repeatedly being washed with water and kneaded with a glass rod, became viscous and finally solidified. It was purified by crystallizing from hot alcohol, from which it is deposited in radial aggregations of fine needles. Fuming nitric acid produces the same result, as was shown by the crystalline form, melting-point and analysis for nitrogen, but it acts more readily. Action began at 60° and rose of its own accord to 75°.

This dinitromethylphenylether is a very yellow compound which dyes the hands and paper yellow. Its alcoholic solution is intensely yellow, and when agitated with water colors it distinctly yellow. It has a slightly bitter taste, and melts at 101°. The mode of formation as well as the analysis for nitrogen would point to its being a dinitromethylphenylether. Found, 10.42 per cent. N; calculated, 10.22 per cent.

NITRO-2-NITRO-2′-METHYL PHENYLETHER.

This was prepared in the same manner as the preceding compound, from the corresponding nitromethylphenylether. It is a sulphur-yellow compound which crystallizes from hot alcohol in well-defined crystals that have very much the same appearance as those of 2-nitro-4′-methyl phenylether. It melts at 98°. An analysis for nitrogen gave 10.42 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-4′-METHYL PHENYLETHER.

This was prepared by the same method as its analogues. It is light yellow in color and changes to a brownish hue on exposure to light. It was purified by crystallizing from alcohol and melts at 100°. An analysis for nitrogen gave 9.95 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-3′-METHYL PHENYLETHER.

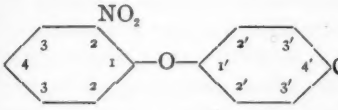
This substance was prepared from the corresponding nitromethylphenylether by the same method as its isomers that have been described. It is yellow and crystallizes from alcohol in radial aggregations of thin plates, which melt at 106°. An accident befell the analysis for nitrogen and there was not enough of the substance at hand to repeat it, but, judging from the fact that the other nitromethylphenylethers have yielded a dinitro derivative under the same conditions, it would seem likely that this is also a dinitromethylphenylether.

HEXANITRO METHYL PHENYLETHER, $(NO_2)_6.CH_3.C_{12}H_3O$.

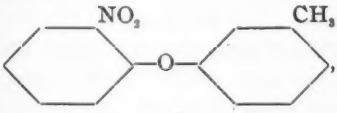
4-Nitro-4′-methyl phenylether was boiled with strong nitric acid for three-fourths of an hour. When the solution was poured into cold water a light yellow oil was precipitated which quickly

solidified. It was purified by crystallization from hot alcohol in which it is very soluble. It is also soluble in benzene, ether, and acetic acid, and sparingly soluble in water. It deflagrates like a nitrate when ignited in the flame of a lamp. Two analyses for nitrogen gave 18.15 and 18.88 per cent. N; calculated, 18.55 per cent.

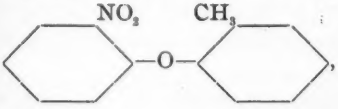
For the sake of greater clearness in comparison the graphic formulas of the six isomeric nitromethylphenylethers are given here:



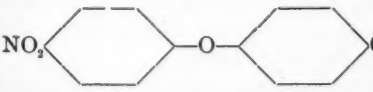
2-Nitro-4'-methyl phenylether: melting-point, 49°; free amino derivative unstable when moist.



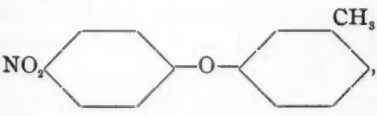
2-Nitro-3'-methyl phenylether: liquid; free amino derivative very unstable when moist.



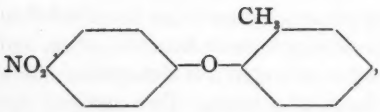
2-Nitro-2'-methyl phenylether: liquid; free amino derivative very unstable when moist.



4-Nitro-4'-methyl phenylether: melting-point, 66°; free amino derivative perfectly stable when moist.



4-Nitro-3'-methyl phenylether: melting-point, 61°–62°; free amino derivative decomposes slightly when moist.



4-Nitro-2'-methyl phenyl-ether: liquid; free amino derivative partially decomposes when moist.

Three of the six isomers are liquids and three are solids. It will be observed that the nearer the nitro and methyl groups are together the greater is the tendency to be a liquid. Of the two intermediate compounds, 4-nitro-2'-methyl phenylether and 2-nitro-4'-methyl phenylether, one is a liquid and one is a solid.

The stability of the free amino derivatives was in proportion to the distance the methyl and amino radicals were apart. The free amino derivative, 4-nitro-4'-methyl phenylether, where the two groups are as far apart as possible, was found to be the most stable. It remained in contact with water for some time without showing any signs of decomposition. 2-Nitro-2'-methyl phenylether and 2-nitro-3'-methyl phenylether where the two groups are as near together as possible are the least stable. They decomposed within a few minutes after being liberated. 2-Nitro-4'-methyl phenylether, where the two groups are one stage further apart, was a little more stable, but it decomposed before it could be dried. The two remaining compounds decomposed only partially while being desiccated.

All of the solid mother-substances are yellow and the liquids are brownish red, due to the presence of the nitro group. Phenylether described by Hoffmeister,[1] and also jointly by Gladstone and Tribe,[2] is a colorless substance. So also are ortho-, meta-, and paracresyl ethers described by the latter chemists.[3]

All of the nitro phenylethers that were examined decomposed when boiled under ordnary atmospheric pressure but distilled unchanged in a good vacuum. This would seem to be due to the oxidizing action of the nitro group, since the original phenylether described by Hoffmeister as well as the ditolyl ethers described by Gladstone and Tribe distil unchanged under ordinary atmospheric pressure. The nitromethyl phenylethers

[1] *Ber. d. chem. Ges.*, **3**, 748.
[2] *J. Chem. Soc.* (1882), p. 6.
[3] *Ibid.*, (1886), p. 25.

with the nitro group in the para position were not examined in this regard but it is quite possible that they would distil under ordinary atmospheric pressure unchanged. Paranitro phenylether described by Haeussermann and Teichmann[1] distilled unchanged at 320°. The boiling-points under diminished pressure lie quite close together, varying from 196° under a pressure of 30 mm. in case of 2-nitro-2′-methyl phenylether to 230°-233° under a pressure of 30 mm. in case of 4-nitro-3′-methyl phenylether.

All are darkened on exposure to light, but not in the same degree. 4-Nitro-4′-methyl ether seems to be the most sensitive to light.

According to Hoffmeister, chromic acid in acetic acid solution does not affect diphenylether on long-continued heating but I have found that it attacks all of the nitro methyl phenylethers in my hands. 2-Nitro-4′-methyl phenylether, however, first yielded a carboxyl acid by oxidation of the side-chain. Repeated attempts to obtain carboxyl acids with the other isomers were not successful.

All yield a monosulphonic acid derivative by warming with concentrated sulphuric acid on the water-bath. The nitromethylphenylethers differ from phenylether in that, as Hoffmeister found, it yielded a disulphonic acid derivative. They were similar in that they seemed to be capable of existing in two modifications. When a solution of one of the sulphonic acid derivatives is evaporated to a small bulk on the water-bath a thick syrupy liquid separates which is of a deep yellow or red color. (This was at first thought to be possibly due to the action of nitric acid, introduced by the addition of lead nitrate to precipitate the excess of sulphuric acid, but lead chloride was substituted with the same result.) If this is dissolved in hot water and allowed to stand, it deposits white or light yellow crystals which, in every case where the determination was made, melted above 100°. None of them were found to be deliquescent as Hoffmeister found his disulphonic acid derivative to be, but one was hygroscopic after desiccation over sulphuric acid. The sulphonic acid of 2-nitro-2′-methyl phenylether, which was the first derivative prepared, and

[1] *Ber. d. chem. Ges.*, **39**, 1446.

which was reported in a previous paper, was obtained only in the syrupy form, but in view of what has been observed since with regard to its isomers, it is very probable that it would also have crystallized, if similar conditions had been supplied. Seven out of ten salts that were analyzed were found to contain water of crystallization, varying from 1 to 4 molecules. Water solutions of all of the acids and salts were more or less yellow whether the acids and salts themselves were yellow or not.

Orthobromnitrobenzene seems to act the most readily upon the potassium cresolates. Parabromnitrobenzene and the potassium cresolates require a continued application of heat for a longer or shorter period.

The specific gravities of 2-nitro-2′-methyl phenylether and 2-nitro-3′-methyl phenylether are about 8.5 per cent. higher than those of diphenylether and ditolyl ether as determined by Gladstone and Tribe and considerably less than that of paranitrophenylether as determined by Haeussermann and Teichman.[1]

There is a marked tendency to crystallize in radial aggregations or warty masses. This property is especially noticeable in the salts of the sulphonic acid derivatives. It was first noted in the barium salt of the disulphonic acid derivative of phenylether, by Hoffmeister.

All yielded a dinitro derivative with great readiness by simply heating with concentrated nitric acid, when they passed into solution. It is possible that some of these substances are identical, since their melting-points, as determined, lie quite close together, *e. g.*, nitro-2-nitro-4′-methyl phenylether, with a melting-point of 100°, and nitro-4-nitro-4′-methyl phenylether, with a melting-point of 101°. Only one of the mother-substances was boiled with concentrated nitric acid for any length of time. It yielded a hexanitro derivative.

Other work is contemplated for the coming year on two or three lines to extend our knowledge of phenylether and its derivatives.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA,
August 30, 1902.

1 *Ber. d. chem. Ges.*, **29**, 1448.

AN INVESTIGATION OF AMMONIO-SILVER COMPOUNDS IN SOLUTION.

By W. R. Whitney and A. C. Melcher.

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I. INTRODUCTION.

This investigation was begun and in large part executed nearly three years ago at a time when much uncertainty existed in regard to the constitution of the ammonio-silver compounds in solution. Its completion and publication was, however, unavoidably delayed, and in the meantime other investigations have been published, which leave no reasonable doubt that these compounds have the formula $(Ag(NH_3)_2)\cdot Cl'$, etc., the silver existing in dilute solution almost wholly in the form of the complex cation $Ag(NH_3)_2^{\cdot}$. This conclusion is confirmed by experiments based on a variety of different principles. Reychler[1] showed that the freezing-point of silver nitrate or sulphate solution is almost unaffected by the addition of ammonia until 2 mols have been added for each atomic weight of silver present, and that subsequent additions then produce the normal lowering, the same as in pure water. Konowalow[2] and Gaus[3] found that silver nitrate and chloride added to a solution of ammonia reduced the partial pressure of the ammonia gas to a value equal to that of a solution of pure ammonia of a concentration less by 2 mols of ammonia for each atomic weight of silver present. Berthelot and Delepine[4] proved by mixing dilute silver nitrate and ammonia solutions that no heat effect resulted upon adding either compound in excess of the amount corresponding to the ratio $1AgNO_3:2NH_3$. Finally Bodländer and Fittig[5] have made a thorough investigation of the solubility of silver chloride and bromide in ammonia solutions of various concentrations and that of the former salt in solutions containing both ammonia and potassium chloride or ammonia and silver nitrate, and by application of the Mass Action Law to the results have shown that the silver is present almost exclusively in the form of the compound $Ag(NH_3)_2\cdot R'$ and its ions. They also

[1] *Ber. d. chem. Ges.*, **28**, 555 (1895).
[2] *Ztschr. phys. Chem.*, **28**, 558 (1898).
[3] *Ztschr. anorg. Chem.*, **25**, 236 (1900).
[4] *Compt. Rend.*, **129**, 326 (1899).
Ztschr. phys. Chem., **39**, 597 (1901).

confirmed this conclusion by measuring the electromotive force of concentration elements composed of silver electrodes in two solutions containing the same concentration of silver nitrate or chloride and different concentrations of ammonia, or the reverse. From both the solubility and electromotive force values they derived the dissociation-constant of the complex ion with reference to its components (Ag and NH_3), and found it to be extremely small.

In spite of these numerous investigations on the subject, it has seemed to us that our own experiments were worthy of publication; first, because they furnish further evidence of the formation of the ion $Ag(NH_3)_2'$ by an entirely independent method—that of electrical transference; second, because many of the experiments involving principles previously applied were made with silver hydroxide instead of with silver salts, so that the data are new ones; and third, because, even when the same compounds and methods were used the confirmation of quantitative data by independent investigators is always of some value.

II. TRANSFERENCE EXPERIMENTS.

Since the conductivity and dissociation of ammonium hydroxide is very slight, and that of the silver and ammonio-silver compounds is comparable with that of other salts, the simple or complex silver ions will alone migrate to an appreciable extent when a solution containing both ammonia and silver salt is electrolyzed. If, therefore, such a solution is placed at the anode end of an electrolysis tube, the rest of which is filled with some other electrolyte (like sodium nitrate), and a current is passed through, and if after a sufficient time the ratio of silver to ammonia is analytically determined in the adjoining and more remote portions of the solution which originally contained neither of these substances, the composition of the complex ion can be determined, provided that only a single kind is formed, and that this does not undergo a considerable dissociation in the absence of its dissociation products.

Experiments of this nature have been made by us on ammonio-silver nitrate and sulphate, with solutions of each salt having two different ratios of ammonia to silver in the anode part of the tube. The apparatus used in these experiments has been previously

described by A. A. Noyes.[1] It consists of two large glass U-tubes which have one of their arms bent at right angles and which are joined beyond the bends by a piece of soft rubber tubing. The inside arms were completely filled, and the outside arms were charged for about 1 cm. in one tube and 4 cm. in the other tube above the top of the lower bends, with a solution of the sodium salt, nitrate or sulphate, having a concentration of one-tenth mol per liter. On the side having the least solution, about 50 cc. of an ammonio-silver solution of known ratio of ammonia to silver and of a concentration in ammonia of 1 mol per liter was now added; and this, owing to its greater specific gravity, immediately sank into the bend. Methyl orange, which had been previously added to the ammonio-silver solution to color it yellow, showed the line of demarkation between the sodium salt solution and the ammonio-silver salt solution and served to give an indication of any possible stirring during the electrolysis. In the case of the nitrate, nitric acid and ammonia were added to the cathode and anode sides respectively, as the electrolysis proceeded, to neutralize the products of the electrolysis, while with the sulphate enough sulphuric acid and ammonia were added at first to neutralize all products which might be formed. Both of these methods of neutralizing the products of electrolysis were tested by electrolyzing a sodium salt solution alone, without the addition of the ammonio-silver solution; in these tests in the arm adjoining the anode the portions were found to remain entirely neutral. When after five hours the electrolysis was stopped, the portions numbered 1-3 were taken from the inside arm beginning Portion 1 about 1 cm. above the line of demarkation. These were analyzed by first titrating the ammonia with nitric acid and then precipitating the silver as chloride, filtering on Gooch crucibles and weighing after drying at 150°. The experimental data are given in Tables I and II. The ratios of the ammonia to silver are expressed in equivalents. The temperature was 25° in all cases. The current used was between 0.15 and 0.20 ampere.

[1] This Journal, **23**, 42 (1901).

TABLE I.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER NITRATE.

Expt. No.	Initial ratio $C_{NH_3} : C_{Ag}$ at anode.	Portion. No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.4625 N HNO_3 used.	Ratio $C_{NH_3} : C_{Ag}$.
1	2.5	1	50	0.5729	17.84	2.065
		2	50	0.5517	17.06	2.051
		3	54	0.3062	9.27	2.008
2	2.5	1	45	0.4784	14.85	2.059
		2	57	0.5921	18.27	2.046
		3	71	0.4850	14.93	2.042
3	3.5	1	40	0.3873	11.99	2.052
		2	48	0.4193	12.79	2.023
		3	61	0.2003	6.19	2.054
4	3.5	1	45	0.4613	14.59	2.097
		2	49	0.5016	15.85	2.096
		3	61	0.4929	15.48	2.082
5	3.5	1	38	0.3990	12.48	2.074
		2	49	0.4882	15.29	2.077
		3	57	0.3722	11.57	2.062

TABLE II.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER SULPHATE.

Expt. No.	Initial ratio $C_{NH_3} : C_{Ag}$. at anode.	Portion No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.2006 N HNO_3 used.	Ratio. $C_{NH_3} : C_{Ag}$.
1	2.5	1	41	0.5065	37.34	2.121
		2	67	0.4862	34.47	2.040
		3	68	0.1034	7.24	2.015
2	2.5	1	41	0.4032	29.57	2.110
		2	59	0.5485	38.44	2.017
		3	68	0.1637	11.29	1.985
3	2.5	1	56	0.5173	37.32	2.075
		2	58	0.4065	28.10	1.989
		3	74	0.0414	2.81	1.95
4	3.5	1	49	0.1700	13.83	2.289
		2	48	0.1377	10.78	2.258
		3	67	0.0616	4.46	2.083
5	3.5	1	45	0.2352	19.91	2.435
		2	44	0.2032	14.95	2.117
		3	62	0.0631	4.47	2.038
6	3.5	1	65	0.5041	40.92	2.335
		2	57	0.3976	29.32	2.121
		3	69	0.0757	5.57	2.117

The atomic ratio of ammonia to silver in each experiment with the ammonio-silver nitrate is almost the same in all portions, but it does have a slightly larger value in the portion nearest the

ammonio-silver solution at the anode. This mean value of the ratio is 2.045 when the original ratio is 2.5, and 2.069 when it is 3.5.

The atomic ratio in the experiments with ammonio-silver sulphate is always higher in the portion adjoining the anode portion than in the more remote ones and considerably larger than 2.0. It is doubtful whether this has any significance, however, for that portion may have been influenced mechanically by the anode portion. The mean value of the ratio in Portions 2 and 3 is 2.000 in the experiments where the original ratio at the anode was 2.5, and 2.122 in those where that ratio was 3.5.

It is evident from all these results that the ammonio-silver ion must have the formula $Ag_n(NH_3)_{2n}$. This is therefore a confirmation of the conclusion drawn from the results by other methods. These experiments furnish, of course, no indication as to the value of n in the formula.

III. FREEZING-POINTS OF SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

The silver oxide, used in the freezing-point and conductivity experiments, was prepared from clear crystals of silver nitrate and chlorine-free potassium hydroxide. It was precipitated from boiling solution and washed with boiling water. Its freedom from silver chloride was proved by dissolving it in nitric acid and subsequently diluting. The ammonia used was made by diluting the commercial chemically pure ammonia of specific gravity 0.90.

The freezing-point determinations were made with the Beckmann apparatus, the usual precautions with reference to the quantity of ice separated and the temperature of the outer bath being observed. The solutions used in the experiments numbered 1-15 in the following table were obtained by saturating ammonia solutions of various concentrations with silver oxide at 25°; the analytical data in regard to them will be found in Table V under the section on Solubility Experiments. The solutions used in the experiments numbered 21 and 22 were not saturated, and were prepared especially for the freezing-point work.

The first column in the table gives the experiment numbers, which correspond to those in Table V. The second and third

columns contain the concentrations in mols of silver and ammonia per 1000 grams of water, calculated on the assumption that the silver exists as $Ag(NH_3)_2OH$ and the remaining ammonia as NH_4OH. The fourth column contains the actual freezing-point of the ammonio-silver solution, while in the fifth column is the freezing-point of the ammonia solution of equivalent concentration, calculated with the constant, 18.6. The rise in freezing-point caused by the addition of silver oxide is given in column 6; and the corresponding decrease in the number of mols present, calculated by using 18.6 as the molecular lowering, is given in column 7.

TABLE III.—FREEZING-POINTS OF AQUEOUS SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

			Freezing-points.			
Experiment No.	Mols AgOH per liter.	Mols NH_3 per liter.	Ammonio-silver solution.	Pure ammonia solution.	Difference.	Decrease of mols present.
1	0.0654	0.214	0.378	0.395	0.017	0.009
2	0.0658	0.220	0.388	0.407	0.019	0.010
3	0.134	0.458	0.838	0.846	0.008	0.004
4	0.140	0.469	0.856	0.866	0.010	0.005
5	0.205	0.671	1.228	1.238	0.010	0.005
6	0.205	0.684	1.244	1.261	0.017	0.009
9	0.251	0.811	1.460	1.496	0.036	0.019
10	0.248	0.827	1.506	1.527	0.021	0.011
11	0.242	0.830	1.500	1.531	0.031	0.017
12	0.257	0.876	1.588	1.616	0.028	0.015
13	0.278	0.899	1.616	1.659	0.043	0.023
15	0.299	0.999	1.820	1.843	0.023	0.012
21	0.111[1]	0.405[1]	0.734	0.748	0.014	0.008
22	0.151[2]	1.063[2]	1.948	1.964	0.016	0.009

A consideration of the magnitude of the values given in column 6 shows that the freezing-point is only very slightly raised even by the addition of considerable quantities of silver oxide. A comparison of columns 3 and 7 shows that the number of molecules, which have disappeared on the addition of silver hydroxide is only, in the extreme case, 4 per cent. of the total number of molecules present. This change is so small that the number of

[1] Ten grams of this solution required 10.67 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 0.1554 gram of silver chloride.

[2] Fifty grams of this solution required 122.71 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 1.0294 grams of silver chloride.

molecules may be said to be unchanged by the solution of silver oxide in the solution. It is evident that this fact is consistent with the formation of the compound $Ag(NH_3)_2OH$ only under the assumption that the dissociation of this compound is substantially complete. In that case for every 2 molecules of ammonia which disappear, 2 new molecules, $Ag(NH_3)_2$· and OH′, are formed. As there were no existing data on the conductivity of ammonio-silver hydroxide, we have investigated it in this direction.

IV. CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

The saturated solution of Experiment 15 (Tables III and V) and four dilutions of it made outside of the resistance cell by means of graduated flasks were used for the conductivity measurements. The ratio NH_3:Ag in this solution was 3.35. As the ammonio-silver hydroxide proved to be a highly dissociated base, the excess of ammonia could have, in its presence, no appreciable conductivity of its own, and it served to reduce any tendency of the complex ion to dissociate into its components. The measurements were made by the usual method of Kohlrausch at a temperature of 24.75°. The conductivities are expressed in reciprocal ohms. The cell-constant determined by means of $^1/_{50}$ molar potassium chloride was 954.8. The results are presented in the following table.

TABLE IV.—EQUIVALENT CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

Liters per mol.	Actual conductivity.	Equivalent conductivity.
3.35	0.0610	194.8
6.69	0.0314	200.5
13.38	0.0159	203.3
26.75	0.00804	205.3
53.50	0.00403	205.8

The equivalent conductivity of completely dissociated silver hydroxide is at this temperature, according to Kohlrausch's values for the separate ion, 258.5.[1] This value is of the same order of magnitude as those given in the table, and it proves that the ammonio-silver hydroxide unlike ammonium hydroxide is a largely dissociated base. This conclusion is further confirmed by the fact that its equivalent conductivity changes only very slightly with increasing dilution. The difference between its value in

[1] See *Sitzungsber. kön. preuss. Akad. der Wissenschaft*, (1901), p. 1031.

$^1/_{58.5}$ molar solution and that of completely dissociated silver hydroxide may well be wholly due to the slower rate of migration of the complex ion and to the usual small proportion of undissociated molecules present at such concentrations even in the case of highly dissociated bases like potassium hydroxide.

The facts that this complex base is nearly completely dissociated and that the freezing-point of ammonia solutions does not change on dissolving silver hydroxide in them show that the composition of the complex compound must be represented by the formula $Ag_n(NH_3)_{n+1}(OH)_n$; for when $(n+1)$ molecules of NH_4OH disappear through combination, this formula evidently requires that $(n+1)$ be reproduced, namely n molecules of OH′ and 1 molecule of $Ag_n(NH_3)_{n+1}$.

V. SOLUBILITY OF SILVER OXIDE, CHLORIDE, AND BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

The silver oxide was prepared as described in Section 3. The silver chloride was prepared in a dark room from silver nitrate crystals by precipitation with potassium chloride, which had been previously twice crystallized from hot water. It was then washed free from chlorides. The silver bromide was made from potassium bromide, which had been boiled for half an hour with bromine to expel all iodine and then crystallized from solution. After washing it free from soluble bromides, it was rotated in a bottle with two successive portions of half-normal ammonia to dissolve any chloride present. The ammonia was made by the distillation from potassium hydroxide of commercial ammonia.

The solutions were saturated by rotating them for six hours or more in the solubility apparatus described by Noyes,[1] the temperature of the bath being kept constant within 0.05°. In the cases of the silver chloride and bromide experiments, the state of saturation was approached both from the undersaturated and the supersaturated side, the two procedures being distinguished by the letters *u* and *s* in the tables below. Since the solubility is greater the lower the temperature, in the former procedure the silver compound was added to the ammonia solution only after it had been brought to the temperature of the bath; in the latter, the solutions were first shaken at 18° for fifteen minutes with an

[1] *Ztschr. phys. Chem.*, 9, 606 (1892).

excess of the salt and then rotated in the thermostat. In the case of silver oxide, the oxide was added to the ammonia at room temperature and then immediately placed in the thermostat for rotation. The experiments were all made at 25°, except that two were made with silver oxide at 0° for the purpose of orientation.

The results are given in Tables V to VII, which are sufficiently explained by the headings.

It will be seen that in the experiments with silver oxide the ratio $C_{NH_3} : C_{Ag}$ is constant within the experimental error throughout the whole range of concentration, even though that of the ammonia varied from about 0.2 to 1.5 molar. In other words, within these limits of concentration the quantity of silver dissolved is almost exactly proportional to the quantity of ammonia in the solution. It has already been shown by Bodländer and Fittig[1] that, assuming the complex compound to be completely dissociated into its two ions, this constancy of the ratio is predicted by the Mass Action Law for any compound of the formula $Ag_n(NH_3)_{n+1}R_n$ and only for one of that formula. As the conductivity measurements of Table IV show that the undissociated portion is relatively small, this constant ratio shows beyond a doubt that the compound in question has this general formula.[2] The mean value of the ratio is 3.314.

In the case of the silver chloride the ratio $C_{NH_3} : C_{Ag}$ varies continuously in value from 13.5 when the ammonia is 2.0 molar to 20.0 when it is 0.028 molar. However, as the solution becomes more and more dilute the values become more nearly constant; and by plotting them a limiting value of 20.20 for the ratio in very dilute solution was obtained.

These results agree fairly well with those of Bodländer and Fittig, who found for 0.1 molar ammonia the ratio 19.7 (our

[1] *Ztschr. phys. Chem.*, **39**, 598.

[2] It is true, to be sure, that the constancy of the ratio $C_{NH_3} : C_{Ag}$ is much more perfect than would be expected theoretically; for a few per cent. of the undissociated compound must be present even in the most dilute saturated solution, and the absolute quantity of this should increase proportionally to the $(n + 1)$ power (instead of the first power) of the concentration of the free ammonia, and thus diminish the value of the ratio. That it does not do so is probably to be attributed partly to the same cause, whatever it may be, that makes strong electrolytes deviate in the same sense from the theoretical dilution law. It may be due in part to a compensation of the theoretical solubility increase by a decrease in solvent power in the more concentrated solutions. How considerable this last may be is shown by the experiments of Konowalow (*Ztschr. phys. Chem.*, **35**, 376) and of Rothmund and Wilsmore (*Ibid.*, **41**, 619).

TABLE V.—SOLUBILITY OF SILVER OXIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4715 N HCl used.	C_{Ag} = atomic weights of silver per liter.	C_{NH_3} = mols NH_3 (total) per liter.	Ratio C_{NH_3} : C_{Ag}.
1	9.18	0.0850	5.37	0.0654	0.214	3.272
2	9.87	0.0917	5.90	0.0658	0.220	3.351
3	10.04	0.1877	12.26	0.134	0.458	3.420
4	9.99	0.1943	12.53	0.140	0.469	3.361
5	10.09	0.2847	18.00	0.205	0.671	3.275
6	9.97	0.2807	18.03	0.205	0.684	3.343
7	14.66	0.4531	28.11	0.225	0.720	3.196
8	13.15	0.4049	25.54	0.224	0.733	3.264
9	10.10	0.3462	21.68	0.251	0.811	3.236
10	10.14	0.3432	22.41	0.248	0.827	3.336
11	14.25	0.4717	30.84	0.242	0.830	3.424
12	14.36	0.5025	32.80	0.257	0.876	3.402
13	10.07	0.3800	23.80	0.278	0.899	3.237
14	9.97	0.3730	23.82	0.276	0.915	3.320
15	25.48	1.0294	66.11	0.299	0.999	3.344
16	10.08	0.4640	29.80	0.343	1.147	3.343
17	10.55	0.6312	40.10	0.454	1.498	3.298
18	10.73	0.6612	41.40	0.470	1.522	3.235
19[1]	....	1.0382	54.02	....	....	2.519
20[1]	....	0.7894	41.39	....	....	2.545

TABLE VI.—SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4625 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weights of silver per liter.	Ratio C_{NH_3} : C_{Ag}.	Method of saturation.
1	47.81	0.9471	193.83	2.042	0.151	13.57	*u*
2	47.01	0.9264	188.76	2.017	0.149	13.51	*u*
3	48.05	0.9431	192.23	2.013	0.149	13.51	*s*
4	46.48	0.9026	184.10	1.991	0.147	13.51	*s*
5	49.24	0.4189	98.51	0.961	0.0616	15.59	*u*
6	47.76	0.3849	91.23	0.916	0.0583	15.71	*u*
7	47.69	0.3850	90.49	0.909	0.0584	15.59	*u*
8	47.93	0.3797	90.37	0.903	0.0572	15.78	*s*
9	48.71	0.3838	91.08	0.896	0.0569	15.73	*s*
10	49.76	0.3825	90.78	0.873	0.0555	15.73	*u*

[1] These two experiments were made at 0° instead of 25°.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4625 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weight of silver per liter.	Ratio C_{NH_3} : C_{Ag}	Method of saturation.
11	48.63	0.3487	83.95	0.863	0.0541	15.97	*s*
12	49.16	0.3507	84.27	0.818	0.0514	15.93	*s*
13	74.52	0.2618	67.95	0.428	0.0249	17.23	*s*
14	76.19	0.2582	67.63	0.416	0.0240	17.37	*s*
15	72.02	0.2338	61.72	0.411	0.0235	17.50	*u*
16	74.89	0.2403	63.43	0.397	0.0227	17.51	*u*
17	144.6	0.2880	78.54	0.253	0.0140	18.08	*u*
18	141.8	0.2830	76.89	0.253	0.0140	18.02	*s*
19	143.7	0.2867	77.66	0.252	0.0140	17.95	*s*
20	142.0	0.2819	76.68	0.252	0.0139	18.04	*u*
21	525.8	0.4656	308.9	0.118	0.00621	18.82	*s*
22	529.1	0.4685	310.1	0.118	0.00621	19.04	*u*
23	504.7	0.4451	295.4	0.118	0.00619	19.09	*u*
24	515.0	0.4590	300.2	0.118	0.00625	18.82	*s*
25	548.6	0.2380	160.8	0.0590	0.00304	19.43	*u*
26	538.0	0.2287	157.6	0.0589	0.00297	19.73	*s*
27	551.9	0.2370	160.5	0.0585	0.00300	19.49	*s*
28	521.2	0.1114	74.73	0.0288	0.00149	19.31	*s*
29	517.8	0.1060	74.01	0.0287	0.00143	20.09	*u*
30	549.3	0.1115	77.96	0.0285	0.00142	20.12	*s*
31	518.1	0.1047	72.73	0.0282	0.00141	19.99	*u*

TABLE VII.—SOLUBILITY OF SILVER BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgBr obtained.	Cc. of 0.2002 N HNO_3 used.	C_{NH_3} = mols NH_3 (total) per liter.	C_{Ag} = atomic weights of silver per liter.	Ratio C_{NH_3} : C_{Ag}.	Method of saturation.
1	605.6	0.1901	1483.0	0.450	0.00170	293.9	*u*
2	591.5	0.1740	1440.0	0.497	0.00159	311.9	*u*
3	617.9	0.1082	817.4	0.268	0.000941	284.7	*u*
4	616.1	0.1223	831.2	0.273	0.00107	256.2	*u*
5	622.3	0.0455	355.8	0.115	0.000391	294.7	*u*
6	625.5	0.0451	365.3	0.118	0.000386	298.3	*u*
7	611.9	0.0316	232.2	0.0764	0.000276	277.0	*u*
8	613.1	0.0303	236.8	0.0777	0.000264	294.5	*u*

value 19.1); for 0.5 molar, the value 18.8 (our value 17.0); for 1.0 molar, the ratio 15.8 (our value 15.5); and for 1.9 molar the ratio 14.0 (our value 13.7).

The fact that this considerable variation in the value of the ratio takes place with the chloride, while there is practically no variation with the oxide, is difficult of explanation. Since ammonium hydroxide is very slightly dissociated and both ammonio-silver hydroxide and ammonium chloride are strongly dissociated, not more than 2-3 per cent. of these latter compounds could be formed by metathesis; and this could therefore not account for the variation. The formation of undissociated ammonio-silver chloride might explain it; but it would be necessary to assume a much larger proportion of it than is usual with di-ionic salts, since the maximum concentration of the complex salt is only 0.15 molar.

In the case of silver bromide where the concentration of the dissolved silver is very small, the ratio shows no progressive variation with the concentration of the ammonia, though this varied from 0.08 to 0.45 molar. Thus for this salt the constancy required by the formula $Ag(NH_3)_{n+1}(OH)_n$ is fulfilled. The mean value of the ratio is 288.8. Bodländer and Fittig, who carried the determinations up to a higher concentration, obtained for the ratio the constant value 321 for ammonia concentrations between 0.193 and 0.574 molar, while for 1.97 molar and for 3.02 molar, the values found were 284 and 260 respectively.

We will next compare the results obtained with the three different silver compounds. It has been shown by Bodländer and Fittig (p. 604 of their article) that, if the electrolytic dissociation is complete and the formula of the complex ion is $Ag(NH_3)_2$, and only in the case of this formula, will the constant ratio of dissolved silver to uncombined ammonia, that is, the ratio $C_{Ag} : (C_{NH_3} - 2C_{Ag})$, in the case of different silver salts, be directly proportional to the solubility of the salts in pure water. And they showed that the results with silver chloride and bromide conformed to this requirement of the theory. As we have investigated a third compound (silver oxide), it is of interest to make a similar comparison in the case of the three compounds. From our values of the ratio $C_{NH_3} : C_{Ag}$ which are 3.314, 20.20, and 288.8 for

the oxide, chloride, and bromide, respectively, we get for the ratio $C_{Ag} : (C_{NH_3} - 2C_{Ag})$ the values $^1/_{1.314}$, $^1/_{18.20}$, and $^1/_{286.8}$. These ratios have been divided by one another in pairs, and the quotients are given in the column headed "ammonia solution" in the table below. The corresponding quotients for the solubilities in pure water are given in the column headed "pure water". The values of the separate solubilities which are used are for silver oxide[1] 216×10^{-6}, for silver chloride,[2] 15.0×10^{-6}, and for silver bromide,[3] 0.71×10^{-6}.

	Ammonia solution.	Pure water.
AgOH : AgCl	13.86	14.40
AgOH : AgBr	218.3	304.2
AgCl : AgBr	15.76	21.13

The agreement of the two values is fairly close in the case of the AgOH : AgCl ratio. In the other ratios, which involve silver bromide, the values are more discordant, owing undoubtedly mainly to an error in the value of the solubility in pure water of this very difficultly soluble salt. If, conversely, this solubility is calculated from those of the other two silver salts in pure water and the ammonia solution ratios, it is found to be 0.99×10^{-6} when the silver oxide is used as a basis, and 0.95×10^{-6} when the silver chloride is so used. The agreement is remarkably good. The mean of these values (0.97×10^{-6}) is probably nearer the truth than that obtained by the conductivity method. Bodländer and Fittig's results and calculations on the relative solubilities in ammonia of the bromide and chloride lead to the value 0.86×10^{-6}, if the solubility of the chloride in water is taken as 15.0×10^{-6}. By the conductivity measurements, Holleman (1893) found 3.3×10^{-6}, Kohlrausch and Rose 2.1×10^{-6}, and Kohlrausch and Dolazalek (1901) 0.71×10^{-6}. By electromotive force measurements Goodwin (1894) found 0.66×10^{-6} and Thiel (1900) 0.81×10^{-6}.

In conclusion, attention may be called to the significance of the experiments on the solubility of silver oxide in ammonia at 0°. The ratio $C_{NH_3} : C_{Ag}$ was found by the two experiments recorded in Table V to have the value 2.53, which is much less than that

[1] Noyes and Kohr : This Journal, **24**, 1146.

[2] Kohlrausch and Rose : *Ztschr. phys. Chem.*, **12**, 242 (1893).

[3] Kohlrausch and Dolazalek : *Sitzungsber. kön. preuss. Akad. der Wissenschaft* (1901), p. 1018.

(3.31) at 25°. In other words, the solubility of silver oxide in ammonia is much greater at 0° than at 25°. This might be due wholly or in part to an increase in the solubility of silver oxide in pure water with decrease of temperature: but this is not the case; for the heat of neutralization of silver oxide with dilute nitric acid is, according to Berthelot, 5,200 calories, while dissolved and completely dissociated bases give the value 13,700 calories, whence it follows that the heat of solution of silver oxide in water is attended by a large absorption of heat, and therefore that its solubility must increase with rise of temperature. The results at 0° therefore show that the complex ion $Ag(NH_3)_2$ is very much more stable at that temperature than at 25°. This is in agreement with the fact, established by Berthelot and Delepine,[1] that a considerable evolution of heat occurs upon mixing dilute silver nitrate and ammonia solutions.

VI. SUMMARY.

It has been shown by this investigation:

(1) That, when an electric current is passed from a solution containing ammonia and silver nitrate or sulphate into an adjoining solution of a neutral sodium salt, an ion of the formula $Ag_n(NH_3)_{2n}$ migrates into the latter solution.

(2) That the freezing-point of ammonia solutions is not changed by dissolving silver oxide in them.

(3) That the equivalent conductivity of ammonio-silver hydroxide is of such magnitude, and changes so slowly with increasing dilution as to show that this compound is nearly completely dissociated.

(4) That it follows from the two facts last stated that ammonio-silver hydroxide has the formula $Ag_n(NH_3)_{n+1}(OH)_n$.

(5) That the solubility at 25° of silver oxide in ammonia solutions is almost exactly proportional to the concentration of the latter between the investigated limits of 0.2 and 1.5 molar; this fact also is consistent only with the formula given in 4. The ratio of the solubility to the ammonia concentration is 1:3.31, both being expressed in equivalents.

(6) That the ratio of the solubility of silver chloride to the concentration of the ammonia decreases (from the initial value

[1] *Compt. Rend.*, **129**, 326 (1899).

1:13.5 at 2.0 molar) as the concentration of the latter decreases, but finally attains at a moderate dilution (about 0.025 molar) a nearly constant value (1:20.2).

(7) That the solubility of silver bromide as previously found by Bodländer and Fittig is proportional to the concentration of the ammonia between the limits of 0.08 and 0.45 molar, and that the ratio has the value 1:289. The constancy of this ratio is in correspondence with the requirement of the formula $Ag_n(NH_3)_{n+1}Br'_n$.

(8) That the ratio of the solubilities in dilute ammonia of silver oxide and chloride is the same as the ratio of their solubilities in water, as the formula $Ag(NH_3)_2 \cdot R'$ alone requires.

(9) That the solubility of silver bromide in water at 25°, is found to be 0.99×10^{-6} and 0.95×10^{-6} when calculated under the assumption of proportionality, from the relative solubilities in ammonia of silver bromide and oxide on the one hand and of silver bromide and chloride on the other.

(10) That the solubility of silver oxide in ammonia is much greater at 0° than at 25°, though the reverse is true of its solubility in pure water; and that this is due to a much slighter dissociation-tendency of the complex ion into its components at the lower temperature.

It is our agreeable duty at this point to express our sincere thanks to Prof. A. A. Noyes for his very considerable assistance and continual interest in this investigation.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 67.]

THE ELECTROLYTIC ESTIMATION OF BISMUTH AND ITS SEPARATION FROM OTHER METALS.[1]

BY ALFRED LEWIS KAMMERER.

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INTRODUCTION.

IN determining bismuth by the ordinary gravimetric methods many difficulties confront the analyst. These limitations led the author to give attention to the estimation of this metal in the electrolytic way.

[1] From the author's thesis for the degree of Ph.D., 1901.

A careful study of the literature was made and all the methods thus far proposed for the electrolytic estimation of bismuth were carefully considered. It was observed that frequent and numerous attempts had been made to determine it electrolytically. As far back as 1840 Cozzi separated bismuth together with other metals from animal fluids. In 1862 Nickels and, three years later, Luckow described methods for its qualitative detection in the presence of other metals. In 1880 Ludwig Schlucht published an important series of investigations on its behavior in electrolysis. From this time on methods for its quantitative estimation began to appear, Luckow, Smith and Classen being the first to do work in this direction. The methods that have been proposed are numerous and diverse in character.[1] The metal has been deposited from oxalic acid and ammoniacal citrate solutions, also from nitric acid, sulphuric acid and phosphoric acid solutions. Mixed electrolytes containing alkaline pyrophosphates, carbonates and oxalates have been employed. Vortmann recommends that the bismuth be deposited together with mercury as an amalgam. More recently Karl Wimmenauer modified the old nitric acid method by introducing glycerine and making use of a revolving anode.

No one of the methods proposed can be said to be entirely free from objection. In fact so doubtful is the successful determination of bismuth electrolytically that Classen does not deem it advisable to describe even one method in the last edition of his book, "Analysis by Electrolysis." Under the heading of bismuth, he merely states, that up to the present time it has been found impossible to precipitate bismuth quantitatively in compact, metallic form.

This lack of success is to be attributed mainly to two causes: (1) the non-obtainment of a dense adherent metallic deposit and (2) the formation of superoxide of bismuth on the anode. The very few methods for which it is claimed that these difficulties have been surmounted introduce other limitations and features quite undesirable, such as the use of very small quantities of metal,

[1] *Literature.*—Luckow: *Ztschr. anal. Chem.*, **19**, 16; Classen and v. Reiss: *Ber. d. chem. Ges.*, **14**, 1622; Thomas and Smith: *Am. Chem. J.*, **5**, 114; Moore: *Chem. News*, **53**, 209; Smith and Knerr: *Am. Chem. J.*, **8**, 206; Schlucht: *Ztschr. anal. Chem.*, **22**, 492; Eliasberg: *Ber. d. chem. Ges.*, **19**, 326; Brand: *Ztschr. anal. Chem.*, **28**, 596; Vortmann: *Ber. d. chem. Ges.*, **24**, 2749; Rüdorff: *Ztschr. angew. Chem.* (1892), p. 199; Smith and Salter: *Ztschr. anorg. Chem.*, **3**, 418; Smith and Moyer: This Journal, **15**, 28; *Ibid.*, **15**, 101; Kollock: This Journal, 1899; Wimmenauer: *Ztschr. anorg. Chem.*, **27**, 1.

the employment of unusual and involved apparatus and the use of solutions difficult to obtain or solutions which do not lend themselves well to the separation of bismuth from other metals. None of these methods offer any advantages over the ordinary analytical methods.

It was with the hope of overcoming these difficulties and eliminating the objectionable uncertainties which always attend the electrolytic determination of bismuth by any of the described methods that the present investigation was undertaken.

Apparatus.—The apparatus used in this work was that usually employed in electrolysis. As cathodes platinum dishes were used of the ordinary shape, having a cathode surface of 100 sq. cm. when containing 150 cc. of liquid. Some had polished interior surfaces, others had their interior surfaces roughened (sand-blasted). Larger dishes, having a capacity of 250 cc., and a cathode surface of 200 sq. cm., were also employed.

The anodes were of two styles, ordinary flat spirals of two turns of stout platinum wire, having an anode surface of 4.5 sq. cm. and basket anodes, having an anode surface of 60 sq. cm. The latter style of anodes has the same shape as the platinum dish which is used as the cathode and is perforated with quite a number of holes to allow free circulation of the electrolyte.

Platinum gauze electrodes were also experimented with. They were in the shape of upright cylinders 5 cm. high and 10 cm. in circumference, the anode surrounding the cathode, and each having an electrode surface of 10 sq. cm. They dipped, or rather, were immersed, into the electrolyte contained in a beaker-glass of 300 cc. capacity.

The advantages offered by gauze electrodes are, briefly, that a very uniform current density is obtained all over the electrode, and therefore a uniform deposit of metal, that the deposit entirely surrounds the wire and, therefore, cannot readily peal off, and finally, that larger currents can be employed, thus reducing the time of deposition.[1]

The current used in these depositions was derived from storage cells.

The heating of the electrolyte was accomplished by means of a

[1] Cl. Winkler: *Ber. d. chem. Ges.*, **32**, 2192; also *Ztschr. anal. Chem.*, **39**, 517.

very small flame of a Bunsen burner. A sheet of asbestos placed a quarter of an inch below the dish shielded it from the direct flame of the burner.

During the electrolysis the dishes were kept covered with cover-glasses having two perforations ground into them. Through one passed the connecting wire of the anode and through the other hung a thermometer which dipped into the electrolyte during the whole deposition so that the temperature could be closely watched.

SOLUTION.

Sulphuric acid, of all the available solutions from which to deposit the metal, seemed to offer the greatest advantages and was therefore selected. As early as 1883 Thomas and Smith[1] and in 1886 Smith and Knerr[2] worked with this electrolyte and with considerable success, but as this was before the introduction of precise measurement of current strength and voltage into electrolytic work, their conditions as to these points are not very definitely stated. In these experiments they limited themselves to the employment of small quantities of metal, which is objectionable as it increases the percentage error.

Having selected sulphuric acid, attention was first directed toward obtaining a solution of bismuth sulphate. The great insolubility of the sulphate and the strong tendency of the dissolved sulphate to form insoluble basic sulphates were difficulties not easily overcome, and the simple sulphate solution was soon abandoned as impracticable. Two determinations, however, were made from simple sulphuric acid solutions obtained as follows: a weighed quantity of bismuth oxide was dissolved in a few cubic centimeters of nitric acid and then evaporated down with concentrated sulphuric acid until fumes appeared, when it was diluted with water and electrolyzed.

In all the subsequent determinations definite volumes of a standardized nitric acid solution of bismuth were employed. The solution was made up as follows: 20 grams (approximately) of bismuth subnitrate were dissolved in 100 cc. of nitric acid (sp. gr. 1.42) and this solution diluted to 1 liter with water. The bismuth content of the solution was then ascertained by cautiously evapo-

[1] *Am. Chem. J.*, **5**, 114.
[2] *Ibid.*, **8**, 206.

rating 20 cc. to dryness in a porcelain crucible and igniting to bismuth oxide (Bi_2O_3) and weighing as such. 10 cc. of such a solution will contain from 0.10 to 0.15 gram of bismuth and 1 cc. of nitric acid.

EXPERIMENTAL PART.

Definite volumes of the standardized bismuth solution were electrolyzed in the presence of free sulphuric acid and an alkali sulphate, the dilution being usually 150 cc.

The effect of the quantity of sulphuric acid on the deposition was studied, also the influence of different alkali sulphates in varying amounts. Further, the effect of variations in the temperature, cathode surface, current density, dilution, and the style of the electrodes received careful consideration. The quantity of nitric acid was also varied and its effect noted.

After making quite a number of experiments in the variation of the quantity of sulphuric acid, 2 cc. of acid of specific gravity 1.84 were found to give the best results. When more acid than that is used it has a solvent influence on the deposited bismuth and makes it almost impossible to precipitate the last traces of the metal.

The presence of an alkali sulphate in solution was found to be essential for obtaining good metallic deposits. In the presence of sulphuric acid alone the metal does not deposit in good form nor completely. Sodium, potassium and ammonium sulphates were experimented with; of the three, potassium sulphate yielded the best results, 1 gram being the most favorable quantity. Sodium sulphate, however, can be used and good results be obtained. In the presence of ammonium sulphate bismuth is deposited in beautiful form, but there is a tendency to superoxide deposition on the anode. Very little of the latter indeed separates, but the slightest quantity is enough to be considered objectionable. The use of ammonium sulphate is therefore not to be recommended.

Larger quantities of nitric acid than that introduced with the standard bismuth solution were found to be objectionable, causing the bismuth to come down loose and black.

It was found that the temperature has considerable influence on the character of the deposit. In the cold it is impossible to precipitate the bismuth in a compact metallic form. On the other hand, when heated to a temperature as high as 70° the electrolyte

exerts a solvent action on the bismuth deposited, making it difficult to completely precipitate the metal. Another objection to high temperatures is the formation of gas bubbles on the bottom of the dish. The bismuth deposits about these in loose, black, spongy masses, which readily become detached and are lost in washing the deposits. If bubbles are noticed, it is advisable to gently tap the dish with the finger, causing them to rise to the surface.

A temperature of from 45° to 50° C. was found to be the most favorable. Roughened cathode surfaces are not advantageous, the bismuth depositing better on polished surfaces.

In all the depositions it was found absolutely necessary to employ a low current strength, especially during the first part of the deposition until most of the metal was precipitated. If a current, much exceeding 0.03 ampere was used as the initial current, the bismuth invariably came down dark and loose. Experiment showed a current strength of 0.02 to 0.05 ampere, depending on the style of electrodes, to be the proper one, the voltage ranging from 1.8 to 2.0 volts. Toward the end of the deposition, when most of the metal has been deposited, the current can be increased to 0.10 to 0.15 ampere to bring down the last traces of bismuth.

The following tables contain the results of determinations made from the different electrolytes after the most favorable conditions for each had been worked out by previous experiments.

Most of the deposits obtained in these determinations were very metallic in appearance, steel-gray in color, usually having the pinkish tinge or caste so characteristic of metallic bismuth. Often the deposited metal was quite crystalline.

The following is a brief statement of the most favorable conditions:

0.10 to 0.15 gram of metal dissolved in 1 cc. of nitric acid (sp. gr. 1.42.)
2 cc. of sulphuric acid (sp. gr. 1.84.)
1 gram of potassium sulphate.
150 cc. total dilution.
Time, 8 to 9 hours.
Temperature, 45° to 50° C.
$N.D._{100} = 0.02$ ampere.
Volts 1.8.

During the last hour the current strength should be increased

BISMUTH FROM SODIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Grams.	Dilution. Cc.	Temperature. °C.	Time. Hours.	N.D.$_{100}$. Ampere.	Voltage. Volts.	Style of cathode.	Character of the deposit.
0.1182	0.1186	2	1	125	50	7½	0.03	1.7	smooth	steel-gray, pink tinge.
0.1182	0.1177	3	1	125	52	7	0.03	1.7	"	
0.1182	0.1190	2	1	125	51	5	0.025	1.7	"	light gray, few black spots.
0.1182	0.1184	2	1	125	55	6½	0.025	1.8	"	same
0.1182	0.1186	2	1	125	43	7	0.02	1.7	"	very light and metallic.
0.1182	0.1177	2	1	125	50	7	0.02	1.7	rough	light gray and metallic.
0.1182	0.1178	2	2	125	45	7¾	0.02	1.7	smooth	" " with few spots.
0.1182	0.1179	3	1	125	53	6¾	0.02	1.7	"	" " " with pink tinge.
0.1182	0.1186	2	1	125	53	7	0.02	1.8	rough	" "
0.1182	0.1193	2	1	125	60	8	0.02	1.8	smooth	" " metallic.
0.1182	0.1180	3	1	125	55	7	0.02	1.7	rough	" " "
0.1182	0.1180	2	1	125	52	8	0.02	1.8	smooth	" " "
0.1182	0.1181	4	1	..	60	8½	0.02	1.7	"	" " "
0.1182	0.1184	4	2	125	66	24	0.02	2.0	"	" " crystalline.
0.1182	0.1186	2	1	125	60	8	0.02	1.8	"	" "
0.1182	0.1180	2	1	125	50	..	0.02	2.0	"	" " metallic.
0.1182	0.1181	2	1	150	45	8	0.02	1.8	"	" "
0.1182	0.1180	2	1	150	45	7½	0.02	1.8	"	" "
0.1182	0.1181	2	1	200	..	..	0.02	..	"	" "
0.0591	0.0590	2	1	150	45	24	0.02	1.9	"	" " metallic.
0.1182	0.1179	2	2	125	..	7½	0.02	1.7	rough	" " "
0.1182	0.1188	2	1	125	60	7	0.02	1.8	"	" " "
0.1182	0.1186	2	1	125	62	7	0.02	2.0	"	" " crystalline.
0.1182	0.1180	2	1	125	50	..	0.02	2.0	smooth	" "
0.1182	0.1176	1	1	125	60	7¼	0.02	1.7	"	" "
0.1434	0.1433	2	1	150	45	22	0.02	2.0	"	dark gray.
0.1434	0.1438	2	1	150	45	9¾	0.02	1.8	"	llght gray.
0.1434	0.1438	2	1	150	45	18	0.02	1.8	"	" "
0.1434	0.1434	2	1	150	45	24	0.02	1.8	"	rather dark.

FROM SODIUM SULPHATE SOLUTION, USING BASKET ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D.$_{100}$ Ampere.	Voltage. Volts.	Character of the deposit.
0.1182	0.1187	2	1	125	6½	60	0.03	2.1	light gray, metallic.
0.1182	0.1171	2	1	125	6¾	55	0.03	2.0	dark, but adherent.
0.1182	0.1176	2	1	125	7	55	0.02	1.8	dark gray.
0.1434	0.1436	2	1	150	22	45	0.02	1.8	light and metallic.
0.1434	0.1436	2	1	150	20	45	0.02	1.8	good, but a little dark.
0.1434	0.1431	2	1	150	18	45	0.02	1.8	light gray.

FROM SODIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D.$_{100}$ Ampere.	Voltage. Volts.	Character of the deposit.
0.1182	0.1181	2	1	200	24	45	0.03	2.0	light gray.
0.1434	0.1433	2	1	200	7	45	0.03	2.0	" " very metallic.
0.1434	0.1434	2	1	200	9¾	45	0.03	2.0	" " " "
0.1434	0.1433	2	1	200	8¾	45	0.03	2.0	" "

FROM POTASSIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D.$_{100}$ Ampere.	Voltage. Volts.	Character of the deposit.
0.1434	0.1428	2	0.6	150	8	45	0.02	1.9	light gray.
0.1434	0.1436	2	0.6	150	9	50	0.02	1.9	" " very metallic.
0.1395*	0.1400	2	1.0	250	9	45	0.025	1.9	" " " "
0.1395	0.1392	2	1.0	150	6½	45	0.02	1.8	" " " "
0.2790	0.2790	2	1.0	150	9	45	0.025	1.9	dark, but adherent.
0.1395*	0.1393	2	1.0	150	6	45	0.02	1.7	light gray.
0.0698*	0.0698	2	1.0	150	7	50	0.02	1.8	" "

* Basket anode.

FROM POTASSIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	Current strength. Ampere.	Voltage. Volts.	Character of the deposit.
0.1395	0.1394	2	1.0	200	8	45	0.06	2	light and adherent.
0.1395	0.1394	2	1.0	200	8	45	0.04	2	" " "
0.1395	0.1393	2	1.0	200	7½	50	0.05	2	dark " "
0.1434	0.1435	2	0.6	200	9	50	0.03	2	light and metallic.
0.1434	0.1435	2	1.0	200	8	55	0.04	2	"
0.1434	0.1431	2	1.0	200	9	50	0.035	2	" " metallic.
0.1434	0.1433	2	1.0	200	8¾	45	0.03	2	" " "
0.1434	0.1430	2	1.0	200	..	45	0.03	2	" " "

FROM AMMONIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Ammonium sulphate. Grams.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D.$_{100}$. Ampere.	Voltage. Volts.	Anodes.	Character of the deposit.
0.1182	0.1186	2	1	125	7	63	0.02	1.8	discolored	light gray and metallic.
0.1182	0.1186	2	3	125	8	60	0.02	1.7	"	" " " "
0.1182	0.1186	2	2	125	30	..	0.02	..	"	" " " "
0.1182	0.1174	2	2	125	7	..	0.02	..	"	" " " "
0.1182	0.1186	2	1	125	8	60	0.02	1.8	not "	" " " crystalline.
0.1182	0.1180	2	1	125	8	60	0.02	1.8	discolored	" " " "
0.1182	0.1189	2	1	125	9	60	0.02	1.8	not "	" " " "
0.1182	0.1179	2	1	125	8½	55	0.02	1.8	" "	light gray.

to 0.15 ampere to bring down the last traces of bismuth. When gauze electrodes are used, such as were described in an earlier part of this paper, a current strength of 0.04 ampere should be used.

Heat is absolutely essential in order to obtain light, metallic deposits. If, however, the electrolysis be conducted two and a half to three hours at 45° C., during which time most of the metal will have been deposited, it may safely be run over night in the cold. This procedure may, in some cases, be more convenient than conducting the electrolysis eight hours during the day at 45° C.

The end of the electrolysis is ascertained by raising the level of the liquid in the dish, or by testing a few drops of the solution for bismuth with ammonium sulphide.

When the metal has all been precipitated, the deposit is washed without interrupting the current. This is done by siphoning off the acid liquid, at the same time replacing it with hot distilled water. When the liquid in the dish is free from acid, the current is interrupted and the liquid poured from the dish. The deposit is washed with a little hot water and drained. It is then rinsed with a little absolute alcohol to remove the remaining water, this treatment being followed by a little ether. Finally the dish is gently warmed over a very small flame until complete evaporation of the ether, when it is desiccated, cooled and weighed.

With a good many deposits it was noticed that the alcohol tended to lift some of the deposited metal and float it away, thus involving loss. This was remedied by substituting for the alcohol a mixture of ether (2 parts) and alcohol (1 part). Treatment with this mixture is followed by anhydrous ether as usual.

When no dehydrating agents are used and the deposit is simply dried in the air by gently warming, an oxidation of the bismuth always takes place, giving high results.

The liquid should be maintained at a constant level during the electrolysis. If the level is raised, a dark border of loosely deposited bismuth forms around the dish, the depth of the liquid added. If the cover-glasses are close-fitting, scarcely any evaporation can take place, so that it is necessary to add but very little water during the electrolysis.

If the conditions as above stated be carefully followed, a good determination can always be obtained.

The problem of the electrolytic estimation of bismuth having been satisfactorily solved, attention was next given to its separation from other metals by the same means. The results of the experimentation in this direction are embodied in what follows.

SEPARATIONS.

(*1*) *Bismuth from Zinc.*—These metals can be separated with ease and precision electrolytically, from sulphuric acid solution. The bismuth comes down in a beautiful compact metallic form in every case free from zinc.

To 10 cc. of a nitric acid solution of bismuth containing 0.15 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) were added 2 cc. of sulphuric acid (sp. gr. 1.84), 0.6 gram of potassium sulphate and a quantity of zinc sulphate equivalent to 0.15 gram of zinc. The solution was then diluted with water to 150 cc. and electrolyzed with a current strength of 0.02 ampere and a voltage of 2.0. The solution was heated to 50° C. The deposition was complete in about eight hours. The same precautions previously observed as to the treatment of the deposited bismuth were of course followed here.

In the following table the results of four determinations are recorded.

RESULTS.

Bismuth taken.	Bismuth found.	Zinc.	Sulphuric acid.	Potass'm sulphate.	Dilution.	Time.	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Cc.	Gram.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1433	0.1684	2	0.6	150	8½	50	0.025	2	basket.
0.1434	0.1430	0.1529	2	0.5	150	8	50	0.02	2	spiral.
0.1424	0.1428	0.1640	2	0.5	150	8½	50	0.025	2	basket.

(*2*) *Bismuth from Cadmium.*—The separation of bismuth from cadmium can also be accomplished with ease and accuracy. The conditions of the separation are very similar to those of bismuth from zinc. A quantity of cadmium oxide equivalent to 0.1500 gram of cadmium was dissolved in 2 cc. of concentrated sulphuric

acid (sp. gr. 1.84). To this solution were added 10 cc. of the bismuth solution containing 0.15 gram of bismuth and 1 cc. of concentrated nitric acid, 1 gram of potassium sulphate and the whole then diluted to 150 cc. Cadmium sulphate or nitrate may be used instead of the oxide. The solution was electrolyzed at a temperature of 50° C. and with a current strength of 0.025 ampere and 2 volts.

In all of the determinations recorded below the bismuth was deposited in light, metallic form, and was absolutely free from cadmium.

RESULTS.

Bismuth taken.	Bismuth found.	Cadmium taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1395	0.1390	0.1500	1	2	150	8	50	0.025	2	basket.
0.1395	0.1400	0.1500	1	2	150	8	50	0.03	2	spiral.
0.1395	0.1400	0.1500	1	2	150	8	45	0.035	2	"
0.1395	0.1396	0.1500	1	2	150	8	45	0.03	2	basket.
0.1395	0.1398	0.1500	1	2	200	8	45	0.035	2	gauze.

(*3*) *Bismuth from Chromium.*—The next separation to receive study was that of bismuth from chromium. The chromium salt used in this case was chrome alum. The presence of chrome alum seems to exert a beneficial influence on the character of the deposit. It is interesting to note that during the electrolysis much of the chromium is oxidized into the condition of chromic acid, the color of the solution changing from green to yellow. On testing the solution, the presence of a large quantity of chromate can be shown. Especially is this the case when gauze electrodes are employed.

The electrolysis was carried out as follows: To a solution of bismuth containing 0.1500 gram of metal and 1 cc. of nitric acid (sp. gr. 1.42) were added, 0.5 gram of potassium sulphate, 2 cc. of sulphuric acid (sp. gr. 1.84) and a quantity of chrome alum equivalent to 0.1500 gram of chromium. This solution was diluted to 150 cc. with water and electrolyzed with a current strength of 0.025 ampere and a voltage of 2.0, the temperature

being maintained at 50° C. After eight hours the deposition was complete and the bismuth was found to be free from chromium.

RESULTS.

Bismuth taken.	Bismuth found.	Chromium.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.$_{100}$	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1430	0.1500	0.5	2	200	9	50	0.03	2	gauze.
0.1434	0.1428	0.1500	0.5	2	150	9	50	0.025	2	basket.
0.1434	0.1434	0.1500	0.5	2	200	8½	50	0.025	2	gauze.
0.1434	0.1428	0.1500	0.5	2	150	8½	50	0.02	2	basket.
0.1434	0.1430	0.1500	0.5	2	150	8½	50	0.02	2	spiral.
0.1434	0.1429	0.1500	0.5	2	150	9	50	0.025	2	"

(*4*) *Bismuth from Nickel.*—Nickel sulphate in quantity equivalent to 0.1500 gram of nickel, 0.5 gram of potassium sulphate, and 2 cc. of sulphuric acid (sp. gr. 1.84) were added to a solution of bismuth containing 0.1500 gram of metal and 1 cc. of nitric acid. This was diluted to 150 cc. with water and electrolyzed with a current of 0.025 ampere and 2 volts, the temperature being 45° C. The bismuth was completely deposited in nine hours and was free from nickel.

RESULTS.

Bismuth taken.	Bismuth found.	Nickel taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.$_{100}$	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1431	0.1500	0.5	2	150	9	40	0.025	2	spiral.
0.1434	0.1430	0.1500	0.5	2	150	9	40	0.025	2	basket.
0.1434	0.1434	0.1500	0.5	2	200	9	45	0.03	2	gauze.

(*5*) *Bismuth from Cobalt.*—The separation of bismuth from cobalt is easily effected. The conditions for their separation are identical with those given under bismuth from nickel. The salt of cobalt used in the following determinations was cobalt sulphate. The deposited bismuth was metallic in appearance and in every case free from cobalt.

RESULTS.

Bismuth taken.	Bismuth found.	Cobalt taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500	0.5	2	150	8¾	45	0.025	2	basket.
0.1434	0.1435	0.1500	0.5	2	150	8½	45	0.025	2	spiral.
0.1434	0.1430	0.1500	0.5	2	200	8½	45	0.03	2	gauze.

(*6*) *Bismuth from Manganese.*—Experiment showed that by this method the separation of bismuth from manganese could be effected without difficulty. The salt of manganese used in this case was manganous sulphate. The following mode of procedure was found to be the best: To a bismuth solution containing 0.1500 gram of metal and 1 cc. of nitric acid (sp. gr. 1.42) add 3 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of manganous sulphate equivalent to 0.1500 gram of manganese. Dilute this solution to 150 cc. with water and electrolyze with a current of 0.025 ampere and 2 volts, keeping the temperature at 45° C. The bismuth will be deposited in nine hours in beautiful form free from manganese.

At first the solution assumes a dark red color due to the oxidation of some of the manganese to permanganate. After an hour or two the color begins gradually to fade away and the solution again becomes colorless. A considerable quantity of hydrated oxide of manganese deposits on the anode during the electrolysis. This deposit was always examined for bismuth but in no case was it found to contain any of this metal.

RESULTS.

Bismuth taken.	Bismuth found.	Manganese taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1438	0.1500	0.5	3	150	23	45	0.025	1.9	spiral.
0.1434	0.1430	0.1500	0.5	3	150	9	45	0.025	2	"
0.1434	0.1435	0.1500	0.5	3	150	9	45	0.025	2	basket.
0.1395	0.1391	0.1500	0.5	3	150	9	45	0.035	2	gauze.

(7) *Bismuth from Uranium.*—Bismuth may be separated from this metal as follows: To a bismuth solution containing 0.1500 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) add 1 gram of potassium sulphate, 2 cc. of sulphuric acid (sp. gr. 1.84) and uranium sulphate equivalent to 0.10 gram of uranium. Dilute this solution to 150 cc. with water and electrolyze with a current strength of 0.025 ampere and a voltage of 2, maintaining the temperature at 45° C. The deposition is complete in eight hours and the deposited bismuth free from uranium.

RESULTS.

Bismuth taken.	Bismuth found	Uranium taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere	Volts.	
0.1395	0.1394	0.1000	1	2	150		45	0.025	2.1	spiral.
0.1395	0.1395	0.1000	1	2	150	8	45	0.03	0.2	basket.
0.1395	0.1399	0.1000	1	2	200	8	45	0.04	0.2	gauze.

(8) *Bismuth from Iron.*—The deposition of bismuth from solutions containing iron is attended with considerable difficulty. Both ferrous and ferric salts were experimented with. The iron present in the solution seems to exert an influence on the bismuth, tending to hold it in solution and prevent its deposition. Especially is this true when the salt used is a ferric salt. This tendency of bismuth to be held in solution is shown even in a more marked degree when the solution contains besides ferric alum an equal quantity of chrome alum. When this is the case, a current of 0.10 ampere will often not cause the slightest precipitation of bismuth. It was thought that this behavior of bismuth could be taken advantage of to separate other metals from it. It was hoped that the bismuth would be held back by the iron and chrome alums and such metals as mercury, copper and silver be deposited from the solution. These hopes were not realized. As soon as another metal is introduced, the condition of affairs is changed, and both the metal and the bismuth are precipitated. Deposits of silver, however, were obtained containing but very little co-

deposited bismuth. Further investigation in this direction might lead to some very interesting and valuable results.

The best conditions for the separation of bismuth from iron were found to be as follows: To the bismuth solution containing 0.15 gram of bismuth and 1 cc. of concentrated nitric acid, add 2 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of ferrous sulphate or ammonium ferric alum equivalent to 0.15 gram of iron. Dilute this solution to 150 cc. and electrolyze at a temperature of 45° C. If a ferrous salt is used, the current strength should be 0.03 ampere, but if a ferric salt is in solution a higher current strength should be employed, 0.05 ampere, the voltage in both cases being 2.0. In eight hours the deposition will be complete. The precipitated bismuth will contain no iron.

In several cases the separation was made in the presence of urea nitrate, but its addition was of no advantage. The same can be said for manganese sulphate, which was also added.

RESULTS.

Bismuth taken.	Bismuth found.	Iron taken.	Urea nitrate.	Potassium sulphate.	Dilution.	Sulphuric acid.	Time.	Temperature.	N.D.$_{100}$.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500[2]	...	0.5	150	2	8½	50	0.025	1.5	spiral.
.....	0.1431	0.1500[1]	...	0.6	150	2	7½	45	0.03	2	"
.....	0.1435	0.1500[1]	...	0.5	150	2	24	45	0.03	2	"
.....	0.1430	0,1500[1]	...	0.5	150	2	24	45	0.03	1.7	basket.
0.1395	0.1394	0.1500[1]	0.5	0.2	150	2	8	45	0.035	2	"
.....	0.1400	0.1500[1]	0.5	0.2	150	2	8	50	0.035	2	spiral.
.....	0.1393	0.1500[1]	0.5	0.2	200	2	8	45	0.05	2	gauze.
.....	0.1397	0.1500[2]	...	0.5	150	2	9	45	0.07	2	spiral.
.....	0.1395	0.1500[2]	...	0.1	150	2	9	45	0.06	2	"
.....	0.1394	0.1500[2]	...	0.1	200	2	8	45	0.06	2	gauze.
.....	0.1395	0.1500[2]	3.0	0.5	150	2	9	45	0.035	2	spiral.

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[1] Ferrous sulphate.
[2] Ferric ammonium sulphate.

THE ALKALOIDS OF ISOPYRUM AND ISOPYROINE.[1]

By George Bell Frankforter.

Received October 16, 1902.

The isopyrum, so far as can be ascertained, has only once been studied chemically. Hartsen,[2] in a brief examination of *isopyrum thalictroides*, reported the isolation of two new alkaloids. The one he named isopyrine and the other he called pseudoisopyrine. The following is a statement of the method which he used in obtaining these two substances: The root of the *thalictroides* was extracted with water and filtered. The filtrate was evaporated almost to dryness and treated with ammonia. The precipitate thus formed, consisted of aluminum hydroxide, tannic acid and the new base, isopyrine. To remove the latter, the precipitate was dried and extracted with ether. By filtering off and evaporating the ethereal solution, the alkaloid was obtained as an amorphous powder. Nothing further was done with the substance. No attempts were made to purify it or to study its properties and no salts of any kind were made.

Pseudoisopyrine, the other alkaloid, was obtained by treating the roots with alcohol, after they had been extracted with water. The alcoholic extract was condensed by evaporation and treated with ammonia as in the case of the aqueous extract. The precipitate formed by the ammonia, was filtered off, dried and extracted with ether. On removing the excess of ether, the alkaloid crystallized out in star-shaped crystals. As in the first case, no attempt was made to purify the substance and no salts were made. The author of the above paper, while applying the above names, suggested that, quite likely, these two substances were known substances, possibly mixtures of the aconite group.

The above paper was published twenty-eight years ago and nothing has been done since that time although the plant is quite abundant in certain localities. According to Gray, isopyrum is abundant throughout the central, northwestern and southwestern states. According to MacMillan,[3] it is widely distributed throughout Minnesota and Iowa.

[1] Read before the American Association for the Advancement of Science, at Denver, 1901.

[2] *Chem. Centrbl.* (1872), p. 523.

[3] "Metaspermae of Minnesota," p. 231.

My attention was first called to the American species, *isopyrum biternatum*, by Professor MacDougal, of Bronx Park, New York, who, in studying the tubers botanically, observed certain reactions which gave evidence of the presence of a substance of unusual interest. A year later, with the assistance of students, enough material was obtained to make a preliminary examination and to prove beyond a doubt, the presence of an alkaloid. The work has been renewed recently, and enough material obtained to make a careful examination. Samples were collected at different times during the summer and examined. That gathered in the early spring contained only a small quantity of the alkaloid, while that gathered later in the summer contained a maximum amount of the alkaloid. In the early spring, the roots appear as fine fibers with only here and there a very small tuber; in midsummer, the tubers were very much larger and more abundant.

The first work done on the American species was to repeat the method given by Harsten on the *thalictroides*. The results, however, were unsatisfactory and other methods were tried and enough of the material was obtained for analysis.

METHOD OF EXTRACTION.

Many methods, including that of Harsten, were tried but with unsatisfactory results. The method which gave best results was as follows: The roots were cleaned, dried, and pulverized and the powder thus obtained, extracted with hydrochloric acid (1:250). The extraction was made first by heating on a water-bath for an hour and then allowing to stand for twelve hours. The acid solution was then filtered off and evaporated to about one-fifth of the original volume and refiltered. The almost clear filtrate was then treated with ammonia. The precipitate formed, which, according to Harsten should contain the alkaloid isopyrine, was saved, dried and extracted with ether. It proved to be only inorganic matter. The filtrate was then evaporated to dryness and extracted with alcohol. The alcoholic solution gave distinct alkaloidal reactions but all attempts to isolate the free base failed.

The roots were now extracted with alcohol in the presence of hydrochloric acid for several hours and filtered. The filtrate was then condensed by evaporation, treated with ammonia, and

filtered. The precipitate thus obtained, was redissolved in hydrochloric acid, reprecipitated with ammonia, and filtered. This filtrate was added to the original filtrate, evaporated to dryness, and extracted with chloroform. The chloroform solution was treated with hydrochloric acid and allowed to stand for several days. At the end of that time, crystals had formed which proved to be the hydrochloride of the alkaloid.

These crystals were removed, purified by filtering through animal charcoal and again crystallized out of water. Thus obtained, the substance was a beautiful white felt-like mass of fine crystals. It is soluble in water and alcohol but almost insoluble in ether.

Under the microscope the crystals appear as long, fine, prismatic needles. The melting-point of the pure substance was found to be 255° to 257° C. The hydrochloride formed a well-crystallized platinum double salt. It is a bright yellow, granular substance, insoluble in water but slightly soluble in alcohol. It melts at 238° C.

THE FREE BASE, ISOPYROINE.

The hydrochloride was dissolved in a very small quantity of dilute alcohol, and sodium hydroxide cautiously added. The white flocculent precipitate formed was filtered off and dissolved in an excess of alcohol. On slowly evaporating the alcohol, the base was reprecipitated as a white, crystalline substance. These crystals had a sharp melting-point of 160° C. On drying at 100° C., the substance lost its crystalline nature and became a light gray powder. Analyses of the dried substance gave the following results:

I. 0.1230 gram of the dried substance gave 0.2814 gram CO_2; 0.0964 gram H_2O.

II. 0.2042 gram of the dried substance gave 0.4628 gram CO_2; 0.1599 gram H_2O.

	Calculated for the formula, $C_{28}H_{46}NO_9$.	Found. I.	Found. II.
Carbon	62.22	62.22	61.81
Hydrogen	8.51	8.70	8.69
Nitrogen	2.54	....	....

In view of the fact that the alkaloid in hand differs widely from

the isopyrine and pseudoisopyrine of Hartsen, the base has been called isopyroine.

ISOPYROINE METHYL IODIDE, $C_{28}H_{46}(CH_3)NO_9I$.

The powder was treated with methyl iodide for two hours on a water-bath with reflux condenser and at the end of that time, the substance, which at first dissolved, formed a yellow residue in the bottom of the flask. The iodide was removed and reprecipitated from an alcoholic solution with water. The substance thus formed was of a yellow color and almost insoluble in water, ether and chloroform. An iodine analysis gave the following numbers:

I. 0.2204 gram of the substance gave 0.0758 gram of silver iodide.

	Calculated for the formula, $C_{28}H_{46}(CH_3)NO_9I$.	Found.
Iodine.....	18.62	18.8

In addition to the iodide, the chloride and the platinum double salt have been made and are in process of analysis.

NEW BOOKS.

THE ELECTRO-PLATING AND ELECTRO-REFINING OF METALS. BY WATT AND PHILIP. New York: D. Van Nostrand Company. 680 pp. Price, $4.50 net.

This new and revised edition of Watt's "Electro-deposition" will be most heartily welcomed by all persons interested in the art of electro-plating and electro-refining. The editor has carefully revised the original work, incorporating in it the most modern advancements in the art, and by the addition of entirely new material has expanded the volume by more than 200 pages.

Two chapters are devoted to preliminary considerations: primary and secondary batteries, and thermopiles, dynamos, the cost of electrical installations of small output for electroplating, etc., etc. A most interesting historical review of electrodeposition constitutes the third chapter, which is followed by 50 pages upon the electro-deposition of copper. Most minute and exhaustive instructions are given. These show everywhere the touch of a master-workman. Gilding also receives ample consideration. Then follow directions for the electro-deposition of

silver, nickel, iron, tin, zinc, platinum, brass, bronze, etc. The chapter on the cost of electrolytic copper refining will appeal to many who are now conducting experiments on this and other metals for commercial purposes.

Thoroughness in detail and exactness in statement of procedure characterize the book. It will prove most helpful to all who use the current for the purposes it so exhaustively treats.

EDGAR F. SMITH.

HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS, with special reference to practical work. By J. W. MELLOR, D.Sc., of Owens College, Manchester, England. Longmans, Green & Co. 1902. xxi + 543 pp. Price, $4.00.

To any one who has followed the latest development of theoretical chemistry, it is clear that the chemist of the future must be also a practical mathematician. The recent successive appearance of several volumes having as one object the application of mathematics to the scientific development of chemistry shows the general recognition of this condition.

Among all these books, none seems to the reviewer more complete or adequate than that at present under discussion. The importance of a concrete conception of mathematical expression is fully realized and continually exemplified, and the arrangement is progressive and logical. "The student of this work is supposed to possess a working knowledge of elementary algebra so far as to be able to solve a set of simple simultaneous equations, and to know the meaning of a few trigonometrical formulas."[1] This scanty foundation is gradually amplified and built upon until the student should find himself a master of practical calculus, and capable of integrating differential equations derived from his own experimentation. Analytical Geometry, Functions with Singular Properties, Hyperbolic Functions, Fourier's Theorem, Determinants, and the Theory of Errors all receive extended discussion. The last-mentioned subject is treated in a particularly lucid and just manner, with especial emphasis upon its limitations, which are too often ignored. At the end of the book are given a collection of useful formulas and tables of reference, including a table of natural logarithms. No space is given to vector analysis, but most chemists will not be troubled

[1] Prologue, p. xx.

by this omission. The emphasis throughout is laid upon that which is practically useful, and the usefulness is illustrated by actual problems taken chiefly from the modern literature of physical chemistry. In general, the book leaves little to be desired, and can be warmly recommended to the many who are in search of a guide more practical than the usual formal treatise upon pure advanced mathematics. THEODORE W. RICHARDS.

TEXT-BOOK OF ELECTROCHEMISTRY. BY SVANTE ARRHENIUS, Professor at the University of Stockholm. Translated by JOHN MCCRAE, PH.D. New York: Longmans, Green & Co. 1902. xi + 344 pp.

The first chapter deals very briefly with the many fundamental conceptions, definitions, etc., necessary to a study of the subject; but the arrangement of this matter could be improved. Polarization is here the first topic touched, and it would seem more logical to let this follow the definitions of atomic weight, of temperature, electrolysis, and other such matters, some of which in fact need not be defined in a book on electrochemistry.

The second chapter is a brief one on the early history of the subject, in which much more space is devoted to the Grotthus theory than to Faraday's facts.

The third chapter covers in a concise and clear manner the laws of gases and of their application in the case of solutions. It has, however, not been shown that van't Hoff's generalization of the gas laws to solutions applies to "all finely dispersed material." Suspensions, at least, may form an exception.

The subject of properties of solutions is then fully treated. Two pages devoted entirely to valency and entitled "Review of Results Obtained," do not seem of use.

The subject of chemical equilibrium is well treated in Chapter VI.

Following the unfortunate lead of Ostwald and of Nernst, Arrhenius considers that the identical light absorption of the various equally dilute permanganate salt solutions is proof of the dissociation theory, and leaves the reader to assume that the color of the ions is a splendid support of the theory. Any one who looks into this point carefully will find it very complicated. The depth of color of salt solutions of colored ions does not change, as does the electrolytic dissociation, with the dilution. In illustrating the

process for determining the transport number, one unfortunate sentence may bother the student a little. Potassium chloride is being electrolyzed and the author states that by analysis after the electrolysis, the increase of potassium about the cathode and of chlorine about the anode enable one to make the calculation. The disposition of the deposited chlorine and potassium should have been discussed here.

The subject of electrochemistry is treated in its widest significance so that many of the physical properties of solutions are carefully considered; therefore, the work practically covers a course on the physical chemistry of solutions as this is now understood.

Two-thirds of the book are devoted to purely electrochemical topics. The treatment of each topic is concise and the selection of topics so complete that it may safely be asserted that no other English work on this subject contains so much in so small space.

The treatment of potential differences, of surface tension, and the mercury electrometers, is well connected. Six pages are devoted to a very fair treatment of the lead accumulator. The Gretz aluminum rectifying cell is also described. Several pages are devoted to practical electrochemical analysis and to copper refining.

Chapter XVII contains brief descriptions of the Peltier and the Thomson Effects, and contains also a couple of pages on the electric arc. There then follow a dozen pages dealing in a practical way with the various classes of the electric furnace and a final discussion of the effect of silent electrical discharges.

Usually when an important discovery is mentioned in the text, an interpolated number refers the reader to the original article. In this way, about 300 original references are made available. In a book of this kind such a scheme is commendable.

Very considerable credit is due to Dr. Euler and to Dr. McCrae for the improvements on the original Swedish work, which was brought up to date and translated into German by the former, and well translated into English and improved with the literature references by the latter.

The mathematics frequently employed do not extend beyond the elements of the calculus.

Because of the breadth of field treated and the general good quality of the treatment, the book is one of the best on the subject. W. R. WHITNEY.

PHYSICS. TEXT-BOOK FOR SECONDARY SCHOOLS. BY FREDERICK SLATE, Professor of Physics, University of California. New York: The Macmillan Co. 1902. xxi + 1414 pp. Price, $2.00.

The seventeen-page preface convinces the reader that the author is preparing a book from a mind trained for teaching natural science. He has clear views as to the pedagogic functions of such a work, and is consistent even to his unwillingness to confuse the mind by pictures of things which can be actually seen in the laboratory. The preface will be instructive to the many teachers who are to read it.

About 100 pages are devoted to the properties of matter; approximately an equal quantity to heat; and the subjects of sound, light, and electricity are also quite fully treated. Besides the index, there is a list of references for collateral reading, an outline of 180 experiments, and a compilation of over 100 interesting questions. The experiments are also especially carefully selected and worded,—there are no cook-book directions. The book is a readable Physics, and is not replete with definitions for the anxious student to commit to memory. He is forced by the arrangement to think for himself. In fact, there is hardly a direct definition in the book. The author's plan is to give the necessary information upon a subject through the discussion of phenomena or of experimental facts, and he usually concludes with a statement that "such a phenomenon is known as diffusion," for example, or "this is called the latent heat". The matter chosen for discussion is well fitted for use with classes of students who are being encouraged to think independently, and is made interesting by the method of presentation. On the other hand, the depth to which each topic has been sounded will prevent even the most advanced of its students from feeling superiority to the treatment. It has evidently been prepared by one who has given the entire subject most careful attention and it should prove to be a very useful book. W. R. WHITNEY.

ESSAYS IN HISTORICAL CHEMISTRY. BY T. E. THORPE. The Macmillan Co.: London and New York. xii + 582 pp. Price, $4.00.

In this book are gathered sixteen addresses which have been

delivered by the author at intervals during the last twenty-eight years. Five of these have been added in the present edition. These are upon: Stanislao Cannizaro; James Watts; Victor Meyer; On the Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century; and On the Development of Chemical Arts during the Reign of Queen Victoria. The style is very delightful and every chemist, and others as well, will find them very interesting and profitable reading. The individuals selected for discussion have been so well chosen that a perusal of the book will give the reader a very considerable insight into the development of chemistry during the last three hundred years.

The last essay of the list is, perhaps, the least satisfactory. While the work of English chemists during Victoria's reign was far from fulfilling the brilliant promise of the first quarter of the nineteenth century, it would certainly be possible to make a better showing for them than the author has here given. W. A. N.

CHEMISCHES PRACTICUM. I. Teil. Analytische Übungen, mit 25 Figuren im Text. By DR. A. WOLFRUM. Leipsic. 1902. xvii + 562 pp. Price, 10 marks.

This book may be considered an attempt at a complete epitome of analytical chemistry, prepared especially for students who expect to devote themselves to chemical technology. It is divided almost equally into three parts, respectively: Qualitative Analysis, Quantitative Analysis, and Technical Analysis. One half of the first part and more than one third of each of the other two parts is given to organic analysis. The whole arrangement is systematic and in every way excellent. Most of the reactions involved, especially in the first part, are explained in accordance with the Ionic Theory.

Generally only one method of analysis is given, but with few exceptions the choice of methods is to be commended. In a few cases the book could have been brought a little closer to date. In the part devoted to technical analysis a brief description is given of the preparation of each metal and chemical product, so that this part of the book is also an epitome of chemical technology.

The fulness of the book is remarkable, for hardly an operation of analytical chemistry is omitted; for example, there are included the analysis of monazite sand, molecular weight determinations

by freezing- and boiling-point methods, toxicological analysis, gas analysis, oil analysis, preparation, analysis and testing of the coal-tar dyes.

When one takes into account the wealth of material compressed into a little more than 500 pages, it is obvious that the treatment cannot be critical nor the directions under each analysis sufficiently explicit to be of value to the student. It would be a good book from which to cram for an examination, and to the chemist it will be a useful book as an index, and outline of the principal processes of analytical chemistry and chemical technology. *Et praeterea nihil.* JAS. LEWIS HOWE.

FIRST BOOK OF QUALITATIVE CHEMISTRY, FOR STUDIES OF WATER SOLUTION AND MASS ACTION. BY ALBERT B. PRESCOTT, PH.D., Director of the Chemical Laboratory, and EUGENE C. SULLIVAN, PH.D., Instructor in Analytical Chemistry, in the University of Michigan. New York: D. Van Nostrand Company. 1902. 148 pp. Price, $1.50.

The plan of the authors of this, the eleventh edition of Professor Prescott's "First Book of Qualitative Chemistry," is given in the preface as follows:

"To enable the beginner in the qualitative laboratory to deal with chemical change in the light of the present studies of *water solution* and of mass action has been the main purpose in preparing this edition. With this intent the little book has been written anew throughout. It was first published by one of the authors in 1879, and designed then as now for classes taking a short course in qualitative practice."

The introduction gives 12 of its 24 pages to such topics as electrolytic dissociation, chemical equilibrium and hydrolysis. If some of these subjects could have been presented as simply as the other topics in the introduction, the book would have been less open to the criticism that the study of qualitative analysis is rendered unnecessarily difficult by presenting it from the standpoint of the dissociation theory. A number of strong arguments against this method of presentation may be given, but the question is not one that can be settled outside the laboratory. The burden of proof rests with the innovators and the present volume will be welcomed as another contribution toward the solution of the problem.

Aside from the debated question, the book has much to commend it. The matter is well arranged. The directions for the study of each analytical group, given under the heading "exercises with the ions," are admirable. They include such instructive experiments as the determination of the delicacy of the various separations and tests.

There are very few inaccuracies in the book. On page 51 in discussing the reduction of compounds of arsenic by means of potassium hydroxide and aluminum, it is stated that phosphoric acid interferes with this test for arsenic through the formation of phosphine. THEODORE WHITTELSEY.

LOGARITHMISCHE RECHENTAFELN FÜR CHEMIKER. VON F. W. KÜSTER. Dritte Auflage. Leipzig: Verlag von Veit and Co. 1902. Price, M. 2.00.

The success of this little book, as shown by the appearance of a second and third edition within a few years, is well deserved. It contains five-place logarithms and four-place mantissas; tables of atomic weights with multiples and logarithms; tables for the calculation of analyses; for the calculation of nitrogen and other gases; constants for molecular-weight determinations; a table for the determination of the volume of a flask from the weight of water or mercury which it contains at 18°; electrochemical constants; solubility of some substances at 15°; and tables for the preparation of normal solutions. The atomic weights used are the most recent, on the basis of O = 16. Unusual pains seems to have been taken to secure accuracy. W. A. N.

THE ANALYSIS OF STEEL WORKS MATERIAL. BY HARRY BREARLEY AND FRED IBBOTSON. Longmans, Green & Co. 501 pp. Price, 14 shillings.

This book is divided into thirteen parts and an appendix. They comprise: I. The Analysis of Steel; II. The Analysis of Pig Iron; III. The Analysis of Steel-Making Alloys; IV. Rapid Analysis at the Furnace; V. The Analysis of Ores; VI. Analysis of Refractory Materials; VII. Analysis of Slags; VIII. Analysis of Fuel; IX. Boiler Water, Boiler Scales, etc.; X. Analysis of Engineering Alloys; XI. Micrographic Analysis of Steel; XII. Pyrometry; XIII. Miscellaneous Notes; Appendix, Bibliography of Steel Works Analysis.

The authors state in their preface that they "have dealt with

the analysis of steel works materials on such lines as could profitably be followed in a busy works laboratory," and that they "believe that the special standpoint from which the book has been written makes it no worse a text-book for technical schools and colleges." The processes given in the books that they have seen either, "(1) are too long and laborious, (2) require too delicate manipulation, (3) are too scanty in their treatment of the newer materials of steel-making, or (4) are not sufficiently accurate."

A series of methods which are not too long and laborious, do not require too delicate manipulation and yet are sufficiently accurate, would indeed be a boon to the profession and would deserve our gratitude and win our admiration. Careful study fails to show a single original method which answers this description or one which is in the smallest degree an improvement on those in use in our American steel works.

The descriptions of the methods for the analysis of steel are generally extremely sketchy and usually lack the details which would make them useful to the student.

For the determination of carbon the authors seem to favor direct combustion of the finely divided sample at a high temperature in a current of oxygen. They recommend sieving the sample to obtain the fine portion and claim that the fine and coarse portions contain the same percentage of carbon. This is contrary to the experience of many skilled analysts. A volumetric method which consists in oxidizing the carbonaceous residue with sulphuric acid and a weighed amount of bichromate, titrating the excess of chromic acid and calculating the carbon is certainly novel. Red lead is recommended as the best reagent for mixing with refractory alloys, such as ferrotungsten, ferrosilicon, etc., although they consider that bismuth trioxide would be preferable but for the price. No description is given of the Eggertz color method. For manganese the bismuthate process is evidently favored. It is an interesting process with points of decided merit.

Many methods are given for the determination of phosphorus but the one recommended by the authors consists in separating the phosphorus as phosphomolybdate, filtering, dissolving in ammonia, acidifying with hydrochloric acid, precipitating with lead acetate, filtering and weighing the lead molybdate, from the

weight of which the phosphorus is calculated. The authors do not refer to the use of the reductor with amalgamated zinc and give no details of the titration with caustic soda, the two methods most largely in use in this country.

The analysis or "Steel-making Alloys" is treated much more satisfactorily, and supplies a want which has existed ever since these alloys have come into general use.

The portion of the book treating of the "Micrographic Analysis of Steel" is clear and well written and is illustrated by well-chosen sections.

An appendix of 145 pages contains "A Bibliography of Steel Works Analysis" by Harry Brearley, which appeared in the *Chemical News*. The references are to English journals only. The other sections of the book call for no particular notice.

The text is occasionally marred by the use of such expressions as "weigh into", and of such words as "filtrable" and "combusted".

The book is clearly printed on excellent paper and is, among works on chemistry, the most creditable specimen of the bookmakers' art that has been issued from the English press for some time.

It contains a full table of contents and an index.

A. A. BLAIR.

INTERNATIONAL CATALOGUE OF SCIENTIFIC LITERATURE. First annual issue. CHEMISTRY. Part I. London: Harrison and Sons, 45 St. Martin's Lane. Price, 21 shillings.

The Royal Society considered, about the year 1893, the advisability of printing a complete index of current scientific literature. It was hoped to do this by international cooperation; therefore, a large number of representative bodies and individuals abroad were consulted. After several meetings of accredited representatives it was concluded to proceed with the publication of such an index. Seventeen branches of science are included in this catalogue. Each complete annual issue will thus consist of seventeen volumes. The price of the set will be about $90. Separate volumes will be sold. The first part of Volume D, devoted to chemistry, has just appeared. It will be followed shortly by a second part. This first volume consists of three sections: (1)

Schedules and indexes in English, French, German and Italian, (2) an author's catalogue, and (3) a subject catalogue. It is evident, from a careful examination of the present volume, that this international undertaking deserves the hearty support and cooperation of all scientific investigators, who will be kept fully and quickly informed of all new discoveries. The chemical volumes will be of real service to all chemists, and the entire catalogue should find a place in every library. S.

QUALITATIVE ANALYSIS, A MANUAL FOR THE USE OF STUDENTS OF CHEMISTRY IN SCHOOLS AND COLLEGES. By L. M. DENNIS, Professor of Analytical and Inorganic Chemistry, and THEODORE WHITTELSEY, Instructor in Analytical Chemistry, Cornell University. Ginn and Co. 1902. pp. 142.

The aim of the authors is to offer "a work in qualitative analysis that shall be both exact and compendious, avoiding on the one hand the diffuseness of the larger treatises and on the other the incompleteness of the smaller manuals." Their method of instruction is to have the student observe the behavior of known substances in solution toward the following reagents: Potassium hydroxide, ammonium hydroxide, sodium carbonate, hydrogen sulphide, ammonium sulphide, hydrochloric acid, and sulphuric acid. This gives the basis for grouping, separation and identification. The analytical methods are generally well chosen and the directions clearly expressed. Following the latter, under the heading "Discussion," are given with suitable fulness the reasons for the various steps and also some consideration of the special difficulties which may be met in practice. The authors have been successful in maintaining a wise balance in the fulness of detail whereby the student receives sufficient information to work intelligently but is still called upon to exercise judgment and discrimination in the application of facts to special conditions. One might wish that the preliminary descriptions were made to include something more than reactions in solution. For example, some statement concerning oxides and their relation to acids, bases, and salts would seem desirable in order that the phenomena of oxidation and reduction might be better understood. It may perhaps be assumed that such information has been secured in a preceding course of general chemistry.

"The Introduction," in the words of the preface, "discusses in

considerable detail the principles and operations involved in qualitative analysis, but it does not include the consideration of the dissociation theory." For this, in the opinion of the writer, the authors are to be distinctly commended. Although the presentation of the ionization theory may accompany not unsuitably the subject of qualitative analysis, yet to base instruction upon it, to translate the statements of fact in so eminently practical a subject into the terms of a theory so hypothetical and still so controverted is, to say the least, not in the interest of sane teaching. The book is commended as one of the best of its class. A. V. E. YOUNG.

THE ELEMENTS OF PHYSICS. By EDWARD L. NICHOLS AND WILLIAM S. FRANKLIN, in three volumes. New York: The Macmillan Company, reprinted 1901. Vol. I, MECHANICS AND HEAT, pp. 220; price, $1.50 (electrotyped 1898.) Vol. II, ELECTRICITY AND MAGNETISM, pp. 272; price, $1.90 (electrotyped 1896).

This work is not intended to include all the aspects of physical instruction. It contains only, as the preface indicates, "concise statements of physical laws, and a systematic development of principles." Without demonstrations of phenomena and an additional course of physical measurements, its excellence must be largely lost upon the student of physics. On the other hand within the compass of its contemplated field, and considering its real date, the work is unusually well balanced and adequate.

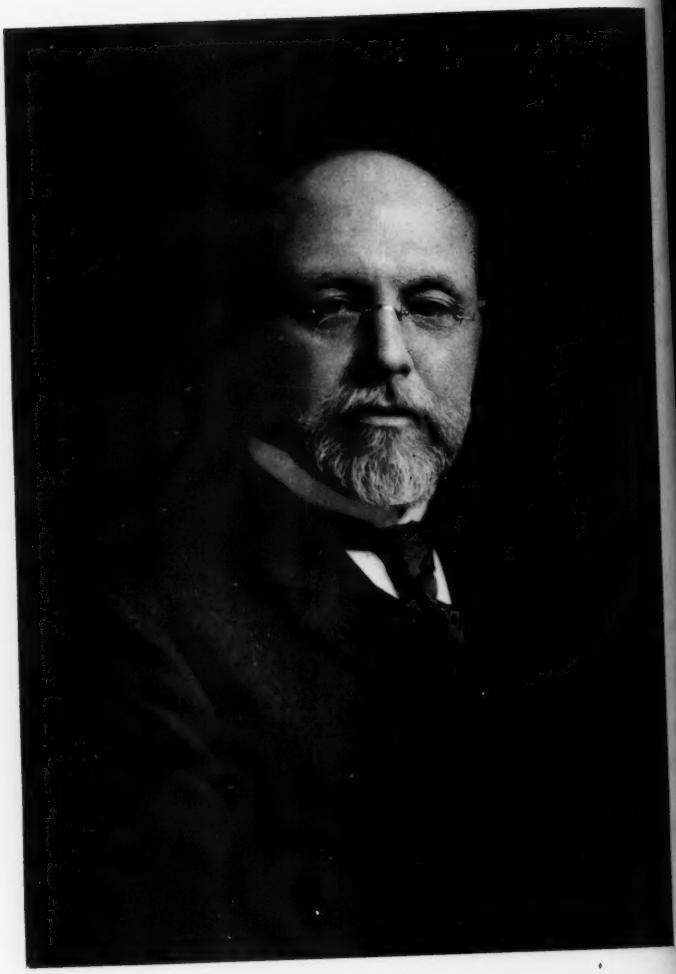
The mathematical method is sufficiently modern, and the lucid explanations of vector calculation and distributed quantity will be helpful to those not already familiar with these concepts. A knowledge of the calculus is of course presupposed. The treatment of physical dimension (in the technical sense) is important and not often so adequately emphasized. In view of this fact it is surprising to find occasionally such an equation as the following, (properly applied, of course, to unit volume): Work = Pressure (Vol. I, p. 117). This type of equation, by ignoring one dimension, seems to indicate the equality of two radically different dimensions. The data are less modern than the treatment. For example the weight of a cubic centimeter of hydrogen is recorded as 0.00008954 gram (Vol. I, p. 179). On page 8 the definition of *mass* does not seem to be convincing, and the importance of Newton's and Bessel's pendulum experiments in showing

the relation between mass and weight seems to have been overlooked.

The second volume of the book is merely a reprint of the edition of 1896; hence, it does not contain descriptions of the Nernst lamp, the Rowland system of telegraphy, or the various practical systems of wireless electrical communication. It is much to be regretted that so good a book should not have been modernized in these respects in the new edition; unless indeed, the real date of the work were made obvious on the title page. Diplex, duplex and quadruplex telegraphy, the telephone, electric furnace, and ordinary electric lighting, are clearly treated. The modern electrochemist will find the treatment of the phenomena with which he is concerned quite inadequate, however.

In general, the work may be characterized as one very useful to him who, already possessing considerable physical knowledge, wishes a more thorough mathematical grasp of those generalizations which have stood the test of time.

THEODORE WILLIAM RICHARDS.



Yours sincerely
Dr. Klemsen.